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ELECTRODE PROCESSES

(*For Table of Contents see page 335*)

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ELECTRODE PROCESSES.

A GENERAL DISCUSSION.

A General Discussion on Electrode Processes was held at the University, Manchester, on Wednesday, 9th April, 1947, from 10 a.m. to 6 p.m., and on Thursday, 10th April, from 10 a.m. to 5 p.m. About 135 members and guests were present, the President, Professor W. E. Garner, F.R.S., occupying the Chair throughout. Among the distinguished overseas visitors the President welcomed the following :—

Mr. Boorboom (The Hague), Dr. H. de Deker (Amsterdam), Mr. T. Førland (Trondheim), Dr. M. Haissinsky (Paris), Dr. J. G. Hoogland (Hengelo), Mr. H. Larson (Norway), and Dr. H. J. C. Tendeloo (Wageningen).

The papers to be discussed had been issued in Advance Proof and were considered under the following main heads :—

I. General and Theoretical.

II. (*a*) Deposition of Hydrogen.
(*b*) Deposition of Metals.

III. Anodic and Other Electrodic Processes.

All the papers and the reports of the Discussion thereon appear in the following pages.

I. GENERAL AND THEORETICAL.

THE CONTACT BETWEEN A SOLID AND A LIQUID ELECTROLYTE.

By T. B. Grimley and N. F. Mott.

Received 25th February, 1947.

The purpose of this note is to examine theoretically the conditions existing in a silver-silver bromide electrode, at the boundary between silver and silver bromide and also at the boundary between silver bromide and the liquid electrolyte. Calculations of the electrode potentials and ζ-potentials are at present in progress, and though not quite complete, it is possible to report at the present stage on the results and general principles involved. The case of silver-silver bromide is chosen as being typical of a much wider class of phenomenon.

§1: The Silver-Silver Bromide Interface.

In this section we shall show how an estimate may be made of the magnitude of the electrical potential difference existing between silver and solid silver bromide. We shall also discuss the charge distribution in the double layer and the difficulties arising in this analysis.

We have to consider first the equilibrium of silver ions in two phases, the metal and the crystal, ignoring for the moment the local properties of the crystal near the interface where, however, the conditions must be assumed to be such that this region itself is a third phase, also in equilibrium. The problem is then that of the equilibrium of a solid and an atmosphere of one of its constituents. The other constituent, the electrons, may be ignored. The atmospheric ions are, of course, not essentially free, but vibrate about fixed lattice points in the crystal. Thus, for a perfect crystal (i.e. one in which the silver ions occupy all their normal lattice points) the partition function for a silver ion is of the form

$$K(T) = \sum_{i=0}^{\infty} p_i \exp(-U_i/kT) \qquad . \quad . \quad . \quad (1)$$

where p_i and U_i are the weights and energies of the vibrational states of the ion in the crystal. Now in silver bromide at ordinary temperatures there exist interstitial silver ions and vacant lattice points (points where a silver ion is missing) and if n_h is the number of vacant lattice points and N' the number of interstitial positions, the partition function for a silver ion in a real crystal splits into two terms and becomes

$$K(T) = n_h \sum_{i=0}^{\infty} p_i \exp(-U_i/kT) + N' \sum_{j=0}^{\infty} p'_j \exp(-W_j/kT) \qquad (2)$$

where p'_j and W_j are the weights and energies of the vibrational states

of an ion in an interstitial position. In the usual theory [1] it is shown that if n_i is the number of interstitial silver ions and N the number of silver lattice sites, then

$$n_i = n_h = \sqrt{(NN')} \exp \{\tfrac{1}{2}(U_0 - W_0)/kT\} \quad . \quad . \quad (3)$$

Here U_0 and W_0 are the energies of the lowest vibrational states of silver ions at lattice sites and interstitial positions respectively. Note that $-U_0$ is the energy required to remove an ion *leaving a hole*.

For silver bromide $(W_0 - U_0) \sim 1$ ev. and since N and N' are of the same order of magnitude we see that the second term on the right hand side of equation (2) is negligible compared with the first so we may write

$$K(T) = n_h \sum_{i=0}^{\infty} p_i \exp(-U_i/kT) \quad . \quad . \quad . \quad (4)$$

If θ_j and E_j are the weights and energies of the vibrational states of a silver ion in metallic silver, and if V_m is the electrical potential of the metal referred to the bulk of the crystal as zero, the partition function for silver ions in the metal is

$$f(T) = \sum_{j=0}^{\infty} \theta_j \exp\{(-E_j - eV_m/kT\} \quad . \quad . \quad . \quad (5)$$

Following the mathematical description employed by Fowler,[2] eqn. (4) may be written

$$K(T) = n_h K'(T) \exp(-U_0/kT) \quad . \quad . \quad . \quad (6)$$

and eqn. (5) similarly becomes

$$f(T) = f'(T) \exp\{(-E_0 - eV_m)/kT\} \quad . \quad . \quad . \quad (7)$$

where E_0 is the lowest vibrational level for a silver ion in the metal. Equilibrium is given by the formula

$$N_l = K(T)/f(T) \quad . \quad . \quad . \quad . \quad (8)$$

where N_l is the number of silver ions at lattice sites in the crystal. N_l may of course be replaced by N the number of lattice sites, then we find

$$eV_m = U_0 - E_0 + kT \log \left\{\frac{N}{n_h} \cdot \frac{f'(T)}{K'(T)}\right\} \quad . \quad . \quad (9)$$

It is reasonable to suppose that the vibrational states of motion of an ion in the crystal and in the metal are very similar so that Fowler's suggestion that $f'(T)/K'(T) \sim 1$ will be a good approximation in this case. To this accuracy eqn. (9) becomes

$$eV_m = U_0 - E_0 + kT \log \frac{N}{n_h} \quad . \quad . \quad . \quad (10)$$

and using eqn. (3) we find

$$eV_m = \tfrac{1}{2}(U_0 + W_0) - E_0 \quad . \quad . \quad . \quad (11)$$

One of us (T. B. G.) has made calculations of U_0 and W_0 using the method first applied by Mott and Littleton to the alkali halides.[3] It was found that $U_0 = -4{\cdot}44$ ev. and $W_0 = -3{\cdot}64$ ev. E_0 may be calculated by the following cycle.

(*a*) Remove a silver atom from the metal. The work required is the lattice energy (W_L).

[1] Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, 1940), p. 28.
[2] Fowler, *Proc. Roy. Soc. A*, 1932, 136, 391.
[3] Mott and Littleton, *Trans. Faraday Soc.*, 1938, 34, 485.

(*b*) Ionise the atom. The work required is the ionisation potential (I).

(*c*) Replace the electron in the metal. The work obtained is the work function of the metal (ϕ).

Then $E_0 = -(W_L + I - \phi) = -5{\cdot}4$ ev.

If therefore the presence of the silver bromide does not appreciably alter this value we derive from eqn. (11) an estimate of the potential difference $V_m \sim 1{\cdot}4$ v.

The concentrations $n_i(x)$ and $n_h(x)$ of interstitial ions and holes at distance x from the interface may be found as follows. If $V(x)$ is the electrostatic potential measured from the bulk of the crystal as zero, we have:

$$n_i(x) = \frac{n_0 \exp\{-eV(x)/kT\}}{1 + s\exp\{-eV(x)/kT\}},$$

$$n_h(x) = \frac{n_0 \exp\{eV(x)/kT\}}{1 + s\exp\{eV(x)/kT\}} \quad . \quad . \quad . \quad (12)$$

where n_0 is the concentration of holes and interstitial ions in the bulk of the crystal and we have written $s = n_0/N$. If the condition

$$s\exp\{\pm eV(x)/kT\} \ll 1$$

is always satisfied, then eqn. (12) reduce to a Boltzmann distribution. For silver bromide, however, $s \sim 10^{-5}$ so we see that such an approximation restricts us to the range where $|eV(x)| < 0{\cdot}3$ v. and it would seem advisable therefore to use the more general expressions as given above. It must be emphasised that the distribution laws of eqn. (12) are themselves in some measure approximate since they do not take into account the dependence of the energies U_0 and W_0 on the concentrations of interstitial ions and vacant lattice points. Such a dependence must certainly be considered in any region where $|eV(x)| > 0{\cdot}3$ v. However, the mathematical difficulties are greatly increased by considerations of this type, in this paper we shall assume eqn. (12) as a sufficiently good approximation. It should be observed that this approximation must correspond closely to reality in so far as an upper limit to $n_i(x)$ and $n_h(x)$ which is of order N is given by eqn. (12).

Poisson's equation now becomes

$$\frac{d^2V}{dx^2} = \frac{8\pi e n_0}{\kappa}\left[\frac{\sinh\{eV(x)/kT\}}{1 + s^2 + 2s\cosh\{eV(x)/kT\}}\right] \quad . \quad . \quad (13)$$

where κ is the dielectric constant of the crystal for static fields. This equation may be integrated once, subject to the condition that $\frac{dV}{dx} \to 0$ as $V \to 0$. Using the condition $s \ll 1$, the result is

$$s\left(\frac{dV}{dx}\right)^2 = \frac{kT}{e}\sqrt{\left(\frac{8\pi e^2 n_0}{4\kappa kT}\right)}\log\{1 + 2s\cosh(eV/kT)\}. \quad . \quad (14)$$

With the assumption that $V = V_m$ when $x = 0$ we have completed the solution for V by solving eqn. (14) numerically. The results are shown in Fig. 1. It must be emphasised that by making this assumption we have excluded any possibility of a rapid change in potential occurring across the first layer of ions in the silver bromide crystal at the contact with metallic silver. An appreciable potential difference of this type may exist in practice, since a relative displacement of the positive and negative ions, in the crystal plane at the interface, over a few tenths of an angstrom is sufficient to set up a potential of $\sim 0{\cdot}5$ v. Unfortunately our knowledge of the short range forces between ions is too uncertain for us to make any reliable calculations on this phenomenon so that,

beyond making this observation, we shall not enter into any further discussion at present.

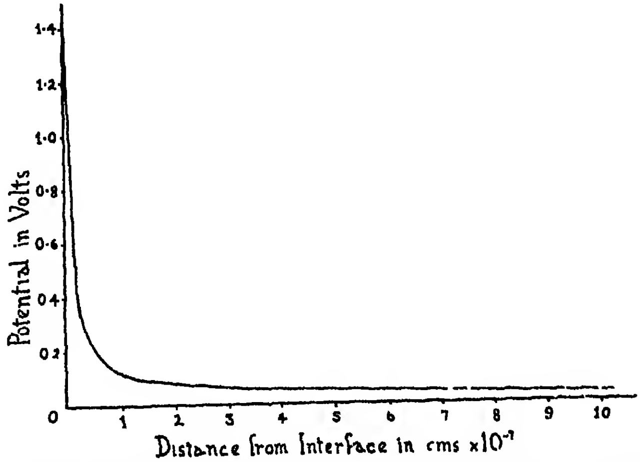

FIG. 1.—Showing how the electrical potential varies near the silver silver bromide interface.

In Fig. 2 we have plotted $n_i(x)$ and $n_h(x)$, the concentrations of interstitial silver ions and vacant lattice points according to eqn. (12). This brings out the essential point of the theory. Namely, that in a region

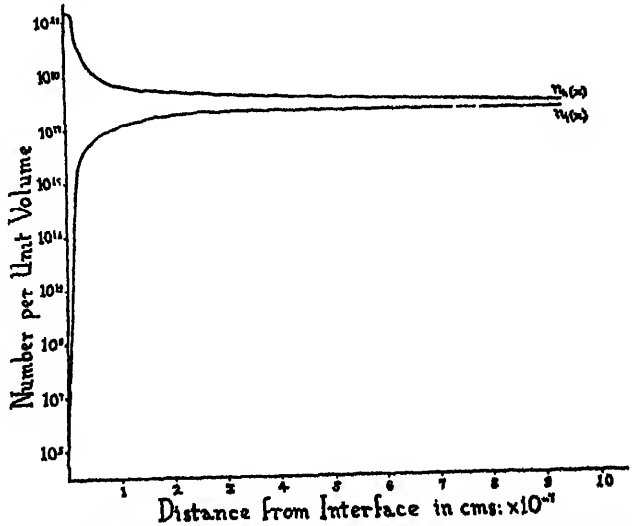

FIG. 2.—The concentrations $n_i(x)$ and $n_h(x)$ of interstitial silver ions and holes near the silver-silver bromide interface.

of the crystal of the order 10^{-6} cm. thick near the interface, the concentration of vacant lattice points exceeds by several powers of ten the concentration in the bulk of the crystal. It is to be expected therefore that the conductivity of a surface layer of this thickness deposited on silver is greatly enhanced.

§2. Contact between Silver Bromide and a Liquid Electrolyte Containing Silver or Bromide Ions.

If silver bromide is placed in an electrolyte of this type, it will, of course, acquire a charge, except at the isoelectric point. Considerations to be published elsewhere, however, show that silver or bromide ions in solution are not appreciably adsorbed actually on the surface of silver bromide, and neither does the crystal carry any significant charge due to a predominance of any type of ion over the other in the crystallographic planes at the interface. The charge resides inside the silver bromide in a layer of the order 10^{-6} cm. thick of the same type as that described above, and is due to an excess of vacant lattice points over interstitial ions or vice versa. In this section we show how the total electrical potential difference between the bulk of the crystal and the bulk of the solution may be calculated, and also how the potential difference between the crystal surface and the bulk of the solution varies with silver ion concentration of the electrolyte.

The total electrical potential difference may be calculated by a method similar to that employed in the calculation of V_m in § 1. We require therefore the partition function for silver ions in the electrolyte. This is [3]

$$\omega(T) = W(1 - 2pc) \sum_{k=0}^{\infty} \omega_k \exp(-H_k/kT) \qquad . \qquad . \quad (15)$$

Here ω_k and H_k are the weights and energies of the vibrational states of a hydrated ion. p is the number of water molecules in the co-ordination shell of a hydrated ion. W is the number of water molecules and c is the concentration of ion pairs in the solution.

Again, following Fowler, eqn. (15) may be written

$$\omega(T) = W(1 - 2pc)\omega'(T) \exp(-H_0/kT)$$

where H_0 is the energy of the lowest vibrational state of the hydrated ion. If V_e is the electrical potential difference between the bulk of the crystal and the solution, the usual condition for equilibrium yields the result

$$eV_e = H_0 - U_0 + kT \log\left\{\frac{c_+}{1 - 2pc} \cdot \frac{K'(T)}{\omega'(T)}\right\} - kT \log\frac{N}{n_k} \quad . \quad (16)$$

where c_+ is the concentration of silver ions in the electrolyte. Here again it is extremely likely that $K'(T)/\omega'(T) \sim 1$ so that eqn. (16) becomes

$$eV_e = H_0 - U_0 + kT \log\left\{\frac{c_+}{1 - 2pc}\right\} - kT \log\frac{N}{n_k} \qquad . \quad (17)$$

Estimates of the individual hydration energies have been made by various authors.[4] In our calculations we have used the result for silver ions given by Verwey.[5] This is $H_0 = -4{\cdot}95$ ev. We have then calculated V_e from eqn. (17) for electrolytes containing various silver ion concentrations and the results are shown in Fig. 3 where V_e is plotted against silver ion concentration.

The concentrations $k_+(x)$ and $k_-(x)$ of positive and negative ions in solution at a distance x from the interface are given by

$$k_+(x) = c\left(\frac{1 - pm}{1 - 2pc}\right) \exp\{-eV(x)/kT\}$$

$$k_-(x) = c\left(\frac{1 - pm}{1 - 2pc}\right) \exp\{eV(x)/kT\} \qquad . \qquad . \qquad . \quad (18)$$

[4] Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515; Latimer, Pitzer and Slansky, *J. Chem. Physics*, 1939, **7**, 108.

[5] Verwey, *Chem. Weekblad*, 1940, **37**, 530.

where $V(x)$ is the electrical potential measured from the bulk of the solution as zero, and for the sake of brevity we have written

$$m = k_{+}(x) + k_{-}(x).$$

Poisson's equation now becomes

$$\frac{d^2V}{dx^2} = \frac{8\pi eN_0}{D}\left[\frac{\sinh\{eV(x)/kT\}}{1 - 2pc + 2pc\cosh\{eV(x)/kT\}}\right] \quad . \quad . \quad (19)$$

where N_0 is the number of ion pairs per unit volume in the bulk of the electrolyte and D is the dielectric constant of the electrolyte. Making the transformations

$$\phi = \frac{eV(x)}{kT}, \qquad z = \sqrt{\left(\frac{8\pi e^2N_0}{DkT}\right)}x$$

and integrating (19) subject to the condition that $\frac{d\phi}{dz} \to 0$ as $\phi \to 0$, we find

$$\left(\frac{d\phi}{dz}\right)^2 = \frac{1}{pc}\log\{1 - 2pc + 2pc\cosh\phi\} \quad . \quad . \quad (20)$$

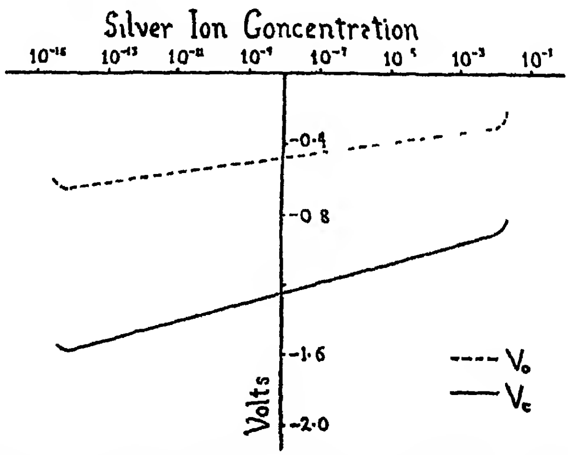

FIG. 3.—Showing how the electrical potential of the bulk of the crystal (V_0) and the crystal surface (V_s) varies with silver ion concentration. The potential of the bulk of the electrolyte is taken as zero.

Similarly, if the electrical potential $V(x)$ on the crystal side of the interface be referred to the bulk of the solution as zero we find

$$\left(\frac{d\psi}{dz'}\right)^2 = \frac{1}{s}\log\{1 + 2s\cosh\psi\} \quad . \quad . \quad . \quad (21)$$

where

$$\psi = \frac{e}{kT}[V(x) - V_s] \quad \text{and} \quad z' = \sqrt{\left(\frac{8\pi e^2n_0}{\kappa kT}\right)}x$$

Since the crystal surface carries no appreciable charge, the dielectric displacement is continuous across the interface between silver bromide and electrolyte. This condition gives the equation

$$\frac{1}{pc}\log\{1 - 2pc + 2pc\cosh\phi_0\} = \frac{\kappa n_0}{DN_0}\frac{1}{s}\log\{1 + 2s\cosh\psi_0\} \quad (22)$$

where ϕ_0 and ψ_0 are the values of ϕ and ψ at the interface. The relation between ϕ_0 and ψ_0 is

$$\phi_0 - \psi_0 = eV_s/kT \quad . \quad . \quad . \quad . \quad (23)$$

Taking the value of the co-ordination number ($p = 6$) used by Verwey [6] in his calculations on the individual energies of hydration we have solved eqn. (22) and (23) for ϕ_0 and ψ_0 in electrolytes of varying silver ion concentrations. The value of ϕ_0 gives immediately the potential V_0 (say)

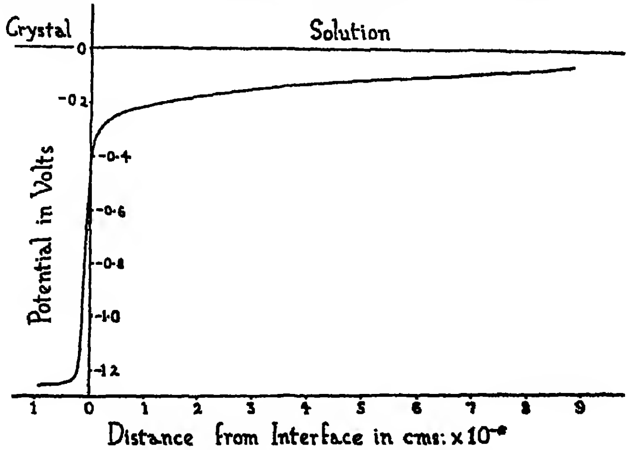

FIG. 4.—Showing how the electrical potential varies with distance on either side of the silver bromide-electrolyte interface, for the case when the electrolyte contains only silver and bromide ions.

of the crystal surface with respect to the bulk of the solution and this quantity is shown plotted against silver ion concentration as the broken curve in Fig. 3.

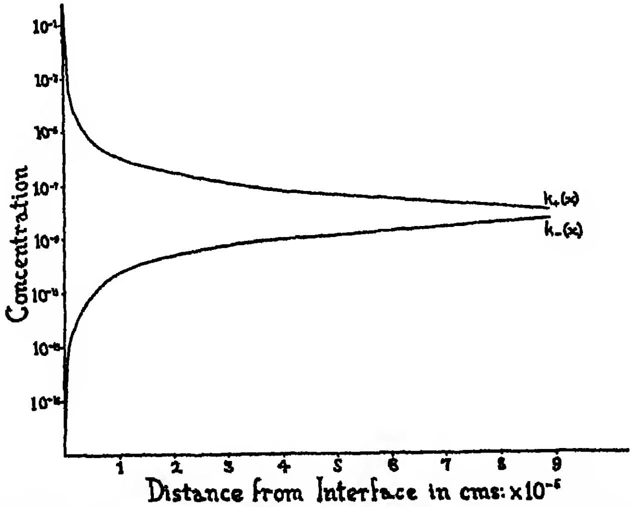

FIG. 5.—The concentrations $k_+(x)$ and $k_-(x)$ of silver and bromide ions in the electrolyte near the silver bromide-electrolyte interface.

Using the values of ϕ_0 and ψ_0 derived from eqn. (22) and (23), eqn. (20) and (21) may be integrated numerically to give $V(x)$ as a function of distance on either side of the interface between silver bromide and electrolyte. We have carried out this integration for the case when the

[6] Verwey, *Rec. trav. chim.*, 1942, 62, 127.

electrolyte consists simply of a saturated solution of silver bromide, and the result is shown in Fig. 4. The concentrations of silver and bromide ions in the electrolyte near the interface were then calculated from eqn. (18) and are plotted in Fig. 5. The concentrations of interstitial silver ions and vacant lattice points in the crystal are given by eqn. (12) and in Fig. 6 we show how, on the basis of this theory, these quantities vary near the silver bromide-electrolyte interface, again for the case when the electrolyte contains only silver and bromide ions.

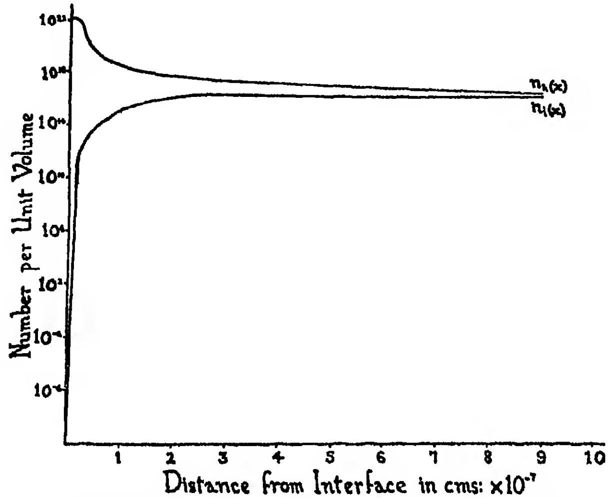

FIG. 6.—The concentrations $n_i(x)$ and $n_h(x)$ of interstitial silver ions and holes near the silver bromide-electrolyte interface.

Conclusion.

As we have indicated previously, the calculations of § 1 are far from complete. In the first place the value of E_0 may be considerably influenced by the proximity of the silver bromide and secondly we have yet to consider the possibility of a rapid potential change, actually at the interface, due to relative displacement of positive and negative ions. We anticipate, however, that in a more detailed theory, where these factors are taken into account, it is unlikely that the whole of the potential difference between silver and silver bromide will be accounted for by the relative displacement of positive and negative ions at the interface so that the general conclusion of § 1, namely, that the conductivity of a thin layer of silver bromide on metallic silver is greatly enhanced, will still hold. The electrical potential difference between the crystal surface and the bulk of the solution, V_0 of § 2 is strictly the true ζ-potential of silver bromide. Although only a portion of this potential difference can probably be measured experimentally by electro-kinetic phenomena we do expect the experimental value to have the same sign as V_0.

From the graph of V_0 in Fig. 3 we see that, according to the calculations of this paper, the ζ-potential of silver bromide should be negative over a wide range of silver ion concentrations. This conclusion is borne out by the work of Julien [7] on streaming potentials in capillaries of fused silver bromide, who found that the negative charge on the capillary could not be reversed by the addition of silver nitrate to the electrolyte. On the other hand, reversal was obtained when the capillary was coated with a

[7] Julien, *Thesis* (Utrecht), 1933.

layer of colloidal silver bromide. This dependence of the electro-kinetic behaviour of insoluble salts on the particle size is well known but so far no quantitative explanation seems to have been given. The present authors would, however, like to point out that when the particle size becomes comparable with the thickness of the charged layer inside the crystal, the method of analysis used in this paper breaks down and more careful considerations are required. It is hoped to return to this question in a later publication.

Résumé.

Les conditions qui règnent (1) à l'interface argent-bromure d'argent solide et (2) au contact entre le bromure et une solution de ses ions, sont examinées d'un point de vue théorique. La différence de potentiel électrique entre l'argent et le bromure d'argent solide est de l'ordre de 1.4v ; la distribution des charges dans la double couche est aussi discutée. Le calcul montre que la concentration des positions vacantes dans le réseau au voisinage de l'interface est très supérieure à celle à l'intérieur du cristal. La seconde partie de l'article traite de la différence totale de potentiel électrique entre le corps du cristal et celui de la solution, ainsi que de la variation de la différence de potentiel entre la surface du cristal et le corps de la solution, en fonction de la concentration des ions argent.

Zusammenfassung.

Die Zustände an den Phasengrenzflächen (*a*) Silber-Bromsilber und (*b*) zwischen Bromsilber und einer Lösung seiner Ionen werden theoretisch untersucht. Es wird geschätzt, dass die elektrische Spannungsdifferenz zwischen Silber und Bromsilber 1·4 v. beträgt. Die Ladungsverteilung in der elektrischen Doppelschicht wird auch besprochen. Berechnungen zeigen, dass die Konzentration von leeren Gitterplätzen in der Nähe der Phasengrenzfläche bei weitem die im Innern des Kristalls übersteigt. Im zweiten Abschnitt wird die Spannungsdifferenz zwischen dem Innern des Kristalls und dem Innern der Lösung ausgearbeitet, sowie auch der Einfluss der Silberionenkonzentration auf die Spannungsdifferenz zwischen der Kristalloberfläche und dem Innern der Lösung.

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KINETICS OF RAPID ELECTRODE REACTIONS.

By J. E. B. Randles.

Received 5th March, 1947.

There are three factors [1] which may operate in controlling the speed of an electrode reaction, (1) the rate of the electrode process itself, (2) the rates of diffusion of the reactant and product, and (3) the ohmic resistance of the electrolyte. Reactions which have received the most study are those for which (1) is very slow, so that rate control due to (2) and (3) has been negligible or has been easily rendered so. A few investigations [2] of moderately rapid electrode processes have been made in which diffusion control has been either disregarded, or minimised. However, most of

[1] Bowden and Agar, *Proc. Roy. Soc. A*, 1938, **169**, 206 ; *Ann. Reports*, 1938, 90.
[2] Erdey Gruz and Volmer, *Z. physik. Chem.*, 1931, **157**, 165. Roiter, Poluyan and Juza, *Acta Physicochim.*, 1939, **10**, 389 ; 845. Essin, *ibid.*, 1942, **16**, 102. Bonnemay, *J. Chim. Physique*, 1944, **41**, 218.

the work on rapid electrode reactions has been done from the point of view of diffusion control alone, the electrode processes themselves being loosely classified as "reversible," i.e. so rapid that their influence on the overall reaction rate can be neglected. Any approach to the measurement of the rates of such electrode processes necessitates as precise as possible a knowledge of rate control due to the combined influence of the electrode process and diffusion. Calculation of this is impeded by the difficulty of solving the dynamic diffusion equation in most circumstances. In the experimental method to be described the working conditions are such as to make possible the solution of this equation.

Theory of the Method.

The basis of the method is the application of an alternating potential of small amplitude to a micro-electrode at which the relevant electrode reaction is proceeding, or is in equilibrium. Let us consider the reaction

$$M^{n+} + ne = M\ (Hg) \qquad (1)$$

occurring between an aqueous solution containing the metal ion M^{n+} at a low concentration C (moles. per cc.), and a solution of the metal in mercury also at a concentration C. (Equal concentrations of M and M^{n+} give the most favourable working conditions and will, for simplicity, be assumed from the start. The effect of inequality of concentrations is discussed briefly in the appendix to this paper.) In order that the diffusion of M^{n+} in the aqueous solution shall not be complicated by migration, a large excess of an indifferent electrolyte such as KNO_3 (concentration molar while C is of the order of 10^{-6} M.) is also present.

Let the mean potential of the electrode be such that reaction (1) is in equilibrium, and let us take this potential arbitrarily as zero. An alternating potential $v = V \cos \omega t$ is now applied between electrode and aqueous solution and in consequence an alternating current will flow which we shall denote as

$$i = I \cos (\omega t + \phi) \qquad (2)$$

where I and ϕ are to be determined. It may be assumed that as a result of this current there will be a harmonic variation in the concentrations of M and M^{n+} close to the interface, which will spread away into the nearby solution. For the concentration C_1 of M in the mercury we may write

$$C_1 = C + \delta C_1$$

and, close to the interface

$$C_1^{\circ} = C + \delta C_1^{\circ} \qquad (3)$$

where

$$\delta C_1^{\circ} = \Delta C_1^{\circ} \cos (\omega t + \theta) \qquad (4)$$

where ΔC_1° is the amplitude of the variation of C_1 close to the interface, and θ the phase angle (relative to the applied alternating potential). A general expression for $\delta C_{1x,t}$ can be obtained by solving the equation for linear diffusion, $\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2}$, for the boundary condition (4) at $x = 0$, x being the distance from the electrode surface (regarded as planar) and D_1 the diffusion coefficient of M in mercury. This gives *

$$\delta C_{1x,t} = \Delta C_1^{\circ} e^{-\sqrt{\frac{\omega}{2D_1}} \cdot x} \cos \left(\omega t - \sqrt{\frac{\omega}{2D_1}} \cdot x + \theta\right) \qquad (5)$$

which represents a diffusion "wave" of length $2\pi\sqrt{\frac{2D_1}{\omega}}$ and whose amplitude declines exponentially with distance from the interface.

* Compare the solution of the corresponding problem in thermal conduction: Carslaw, *Conduction of Heat in Solids* (Macmillan, 1921), p. 47.

The current flowing (taking a positive value of i corresponding to the left to right direction of reaction (1)) is given by

$$i = -nFAD_1\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = -nFAD_1\left(\frac{\partial(\delta C_1)}{\partial x}\right)_{x=0}$$

where F is the Faraday and A the area of the electrode. Using (5) we obtain

$$i = nFAD_1\Delta C_1^\circ\sqrt{\frac{\omega}{2D_1}}\,[\cos(\omega t + \theta) - \sin(\omega t + \theta)] \quad . \quad (6)$$

$$= nFA\Delta C_1^\circ\sqrt{\frac{\omega D_1}{2}}\cos\left(\omega t + \theta + \frac{\pi}{4}\right). \quad . \quad . \quad . \quad (7)$$

Hence $$I = nFA\Delta C_1^\circ\frac{\sqrt{\omega D_1}}{2}; \qquad \phi = \theta + \frac{\pi}{4}. \quad . \quad . \quad . \quad (8)$$

Comparison of (7) with the corresponding expression based on the diffusion of M^{n+} in the aqueous solution, shows that

$$-\frac{\Delta C_1^\circ}{\Delta C_2^\circ} = \sqrt{\frac{D_2}{D_1}}$$

where subscript 2 indicates quantities appertaining to M^{n+}. Since[3] D_2 is generally approximately equal to D_1 we shall assume that

$$\Delta C_2^\circ = -\Delta C_1^\circ \quad . \quad . \quad . \quad . \quad . \quad (9)$$

the minus sign showing that they are 180° out of phase. Having assumed $D_1 \approx D_2$ we shall from now on omit the subscript on D.

The current may also be expressed in terms of the rates of the two opposing processes of equation (1), as

$$i = nFA[k_2C_2^\circ e^{\alpha vnF/RT} - k_1C_1^\circ e^{-(1-\alpha)vnF/RT}] \quad . \quad . \quad (10)$$

where C_1° and C_2° are the respective concentrations of M and M^{n+}, close to the interface, k_1 and k_2 are the rate constants for the two reactions, v is the potential of the aqueous solution relative to the mercury and α is the fraction of the potential difference operative on the aqueous solution side of the energy barrier.[4] Since we are taking v as zero for the equilibrium potential of the electrode when $C_1^\circ = C_2^\circ = C$, then $k_1 = k_2 = k$ where k defines the rates of the opposing reactions at the equilibrium potential as kC moles per sec. per unit area of electrode surface. Substituting for C_1° and C_2° by means of (3) and (9), (10) becomes

$$i = nFAk[(C - \delta C_1^\circ)e^{\alpha vnF/RT} - (C + \delta C_1^\circ)e^{-(1-\alpha)vnF/RT}] \quad . \quad (11)$$

We now use (6) and (11) to obtain ΔC_1° and θ. It is convenient first to differentiate both with respect to time. Provided that nvF/RT is small ($< 0{\cdot}2$), then to a close approximation, and independent of α (but the approximation is closest if $\alpha \approx \frac{1}{2}$), equation (11) leads to

$$\frac{di}{dt} = 2nFAkC\left(\frac{nF}{2RT}\frac{dv}{dt} - \frac{1}{C}\frac{d(\delta C_1^\circ)}{dt}\right)$$

$$= 2nFAkC\left[-\frac{nF}{2RT}\omega V\sin\omega t + \frac{1}{C}\Delta C_1^\circ\,\omega\sin(\omega t + \theta)\right] \quad . \quad (12)$$

From (6) we have

$$\frac{di}{dt} = -nFA\Delta C_1^\circ\sqrt{\frac{\omega D}{2}}[\omega\sin(\omega t + \theta) + \omega\cos(\omega t + \theta)] \quad . \quad (13)$$

[3] Kolthoff and Lingane, *Polarography* (Interscience, 1941), p. 151; *Landolt Bornstein Tabellen*, 5th Ed., I, 249.

[4] Glasstone, Laidler and Eyring, *Theory of Rate Processes* (McGraw-Hill, 1941), p. 575, etc.

Expanding (12) and (13) and equating coefficients of $\cos \omega t$ gives

$$-\cot\theta = 1 + \frac{2k}{\sqrt{\omega D}}$$

whence

$$\cot\phi = 1 + \frac{1}{k}\sqrt{\frac{\omega D}{2}} \quad . \quad . \quad . \quad . \quad (14)$$

Thus ϕ may vary from zero to $\frac{\pi}{4}$ according as $\frac{1}{k}\sqrt{\frac{\omega D}{2}}$ varies from infinity to zero.

Equating coefficients of $\sin \omega t$ in (12) and (13) leads to

$$\Delta C_1^\circ = -\frac{kCnFV}{RT}\sqrt{\frac{2}{\omega D}}\sin\theta = \frac{nFCV}{\sqrt{2}RT}\sin\phi$$

whence

$$\frac{I}{V} = \frac{n^2F^2AC\sqrt{\omega D/2}}{RT}\sin\phi \quad . \quad . \quad . \quad . \quad (15)$$

For a rapid reaction (k large), (15) becomes $n^2F^2AC\sqrt{\omega D}/2RT$ depending on D but not on k, while for k small it becomes n^2F^2ACk/RT.

Since the current vector I leads the voltage vector V by an angle ϕ it is convenient to compare the system with its electrical equivalent, a condenser and resistance in series. Denoting these by C_s and R_s we have

$$\frac{I}{V} = \frac{1}{R_s}\cos\phi, \qquad \omega C_s R_s = \cot\phi.$$

By means of (14) and (15) the following relations are derived

$$R_s = \frac{RT}{n^2F^2AC}\left(\sqrt{\frac{2}{\omega D}} + \frac{1}{k}\right) \quad . \quad . \quad . \quad . \quad (16)$$

$$C_s = \frac{n^2F^2AC}{RT}\sqrt{\frac{D}{2\omega}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and

$$R_s - \frac{1}{\omega C_s} = \frac{RT}{n^2F^2AC}\cdot\frac{1}{k} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Measurement of R_s and C_s will therefore enable the rate constant k to be calculated.

Experimental.

Apparatus.—The micro-electrode used was a capillary dropping electrode similar to a polarographic electrode except that a dilute amalgam replaced the mercury. Such an electrode has the advantages that its surface is continually renewed, and that the surface area is easily measured by weighing the drops. The amalgams were prepared by electro-deposition of the required amount of metal from solution, on to a measured volume of mercury acting as cathode, in the apparatus shown in Fig. 1. The electrolyte was generally NH_4Cl solution with the appropriate amount of metal salt added. A mercury anode was used, contained in a small glass cup filled up with KNO_3 solution and with a loose cotton-wool plug inserted. During the electrolysis the counter migration of mercurous ions, and Cl′ ions from the main electrolyte, precipitated Hg_2Cl_2 in the cotton wool thus preventing the entry of mercury ions into the main electrolyte but avoiding the contamination of the mercury surface. Air was displaced from the electrolysis vessel by nitrogen. The amalgam was used direct from the vessel by means of the long capillary syphon shown in the diagram, the negative potential of the amalgam relative to the electrolyte being maintained in order to prevent re-solution of the dissolved metal.

Electrical measurements were carried out with the capillary electrode immersed in a suitable solution contained in a cell of the type used in polarography. The other electrode was a mercury pool, and an auxiliary electrode of platinum gauze was fitted over the lower end of the capillary, flush with the end as shown in Fig. 1 (*a*). The solutions contained indifferent electrolyte (KNO_3, KCl, etc.) at molar concentration and a low concentration (of the order of 10^{-3} M.) of the ion under investigation. Atmospheric oxygen was expelled by a stream of nitrogen. The cell was placed in a thermostat at 25° ± 0·1° C.

The electrical circuit is shown in Fig. 2; D.E., G.E., and M.P. are the dropping electrode, gauze electrode and mercury pool electrode respectively. A valve oscillator connected to points A and B supplied alternating current of adjustable frequency. The current passed by the dropping electrode flowed also through the variable resistance *R* and the variable capacity *C* (a set of standardised condensers). The potential difference across *R* and *C* was amplified by a D.C. push-pull amplifier connected to XX, the output of which was applied to one pair of deflector plates of a cathode ray tube. The potential difference between the dropping electrode and the gauze electrode was similarly amplified and applied to the other pair of deflector plates. A negligible current flowed through the gauze electrode therefore its potential followed exactly that of the surrounding solution. By making the distance between it and the dropping electrode as small as possible the minimum of potential drop due to electrolyte resistance was included in the measured potential difference. The mercury pool was connected to *R* and *C* and the dropping electrode to earth in order to avoid the difficulty of electrical screening of the latter.

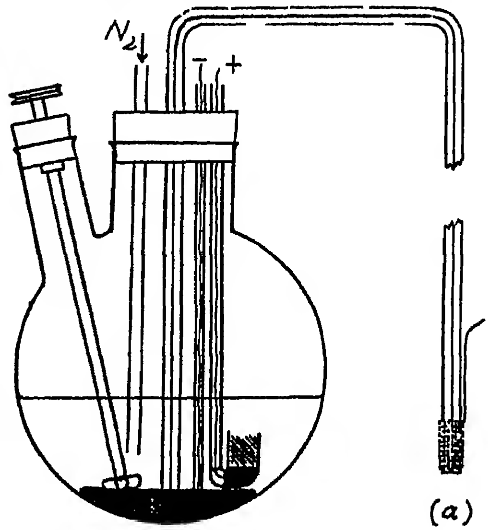


FIG. 1.

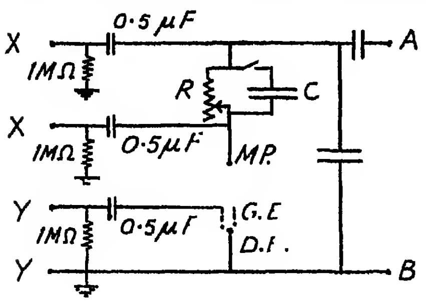


FIG. 2.

Method of measurement and calculation of results.—With capacity *C* zero and resistance *R* in the circuit the cathode ray trace is an ellipse. By switching out one amplifier at a time, the horizontal and vertical amplitudes for maximum size of the amalgam drop were measured. When corrected for overall sensitivity for the two directions the ratio of these amplitudes gives RI/V where R is known. The total voltage swing, $2V$, never exceeded about 7 mv. as required in the derivation of equation (12). The voltage-current phase difference, ϕ', for the dropping electrode-gauze electrode was obtained by adjusting C and R until the trace became a straight line at maximum drop size. The phase angle

for the C-R combination given by $\tan \phi' = \omega CR$ is then equal to that for the electrode system.

The whole electrode system is electrically equivalent to the circuit shown in Fig. 3 (*a*), where C_r and R_r are the capacity and resistance equivalent to the electrode reaction, C_l the ordinary double layer capacity of the electrode surface and R_c the electrolyte resistance between the electrode and the platinum gauze. R_c was obtained by measuring the total impedance, with the usual indifferent electrolyte, but cutting down the impedance due to C_r and R_r to about 3 ohms by using a high (M./20) concentration of lead or cadmium in the amalgam and solution. Thirty ohms is a typical value for R_c. C_l was measured in a series of experiments using pure mercury and pure indifferent electrolyte for various potentials of the electrode; values of C_l per unit area agreed well with accepted values.

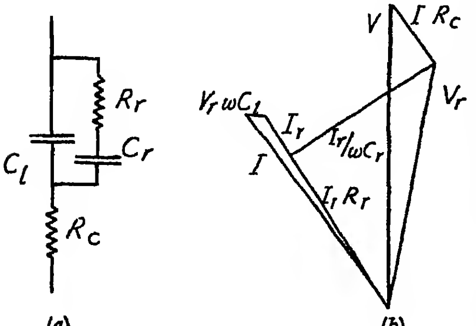


FIG. 3.

A vector diagram, Fig. 3 (*b*), was used for calculating C_r and R_r. Measured values of V and I are first drawn at angle ϕ'. A vector IR_c, parallel to I is subtracted from V giving V_r. $V_r\omega C_l$, normal to V_r, is subtracted from I giving I_r. A normal from V_r to I_r gives the values of I_rR_r and $I_r/\omega C_r$, from which R_r and $1/\omega C_r$ are calculated.

Results.

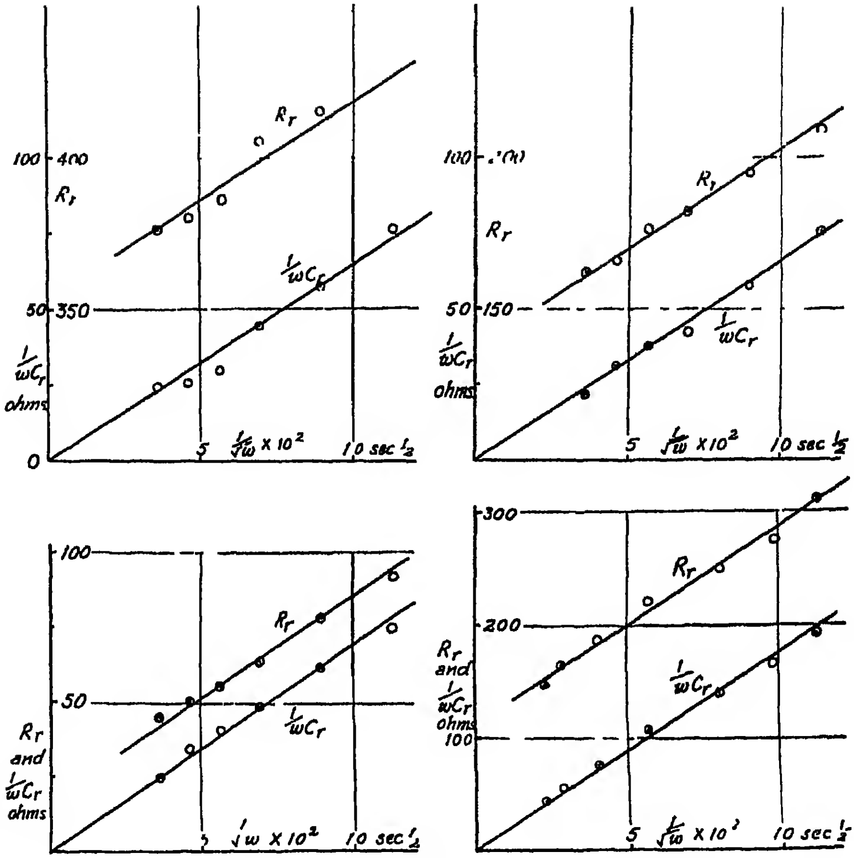
The results presented in this section are exploratory in character and much more extensive work is intended. Only a few metal-metal ion reactions have been investigated. However, the data obtained is sufficient to verify the theoretical equations and to illustrate the type of result obtainable.

Expressions (16) and (17) show that R_r and C_r plotted against $1/\sqrt{\omega}$ should give straight lines. Instead of C_r it is more profitable to plot the capacitative impedance $1/\omega C_r$ which should give a straight line through the origin parallel to the R_r line, and at a distance from it given by (18). Results for copper, zinc, cadmium and thallium are plotted in Figs. 4 and 5. The dotted lines in the cadmium and thallium graphs are those calculated for $\frac{1}{\omega C_r} = \frac{RT}{n^2F^2AC}\sqrt{\frac{2}{D}} \cdot \frac{1}{\sqrt{\omega}}$, using for D the geometric mean of the diffusion coefficients of the ion in water and the metal in mercury, i.e.

$$\sqrt{0{\cdot}65 \times 1{\cdot}5} \times 10^{-5} \text{ and } \sqrt{2{\cdot}0 \times 1{\cdot}0} \times 10^{-5}, \text{ cm.}^2 \text{ sec}^{-1}.,$$

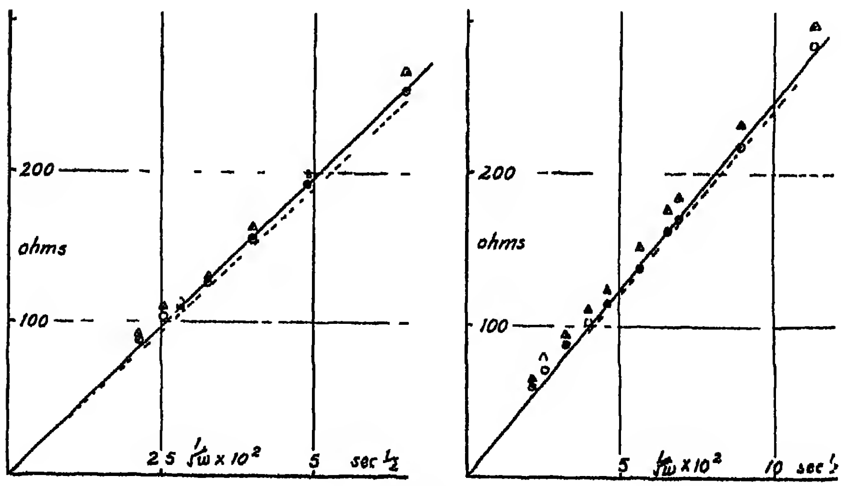
for cadmium and thallium respectively.

Inspection of the graphs shows that constancy of $\left(R_r - \frac{1}{\omega C_r}\right)$ is satisfactory for the reactions of moderate rapidity but it is not so good for the very rapid reactions (cadmium and thallium). This is only to be expected as in the latter case it represents a small difference between two comparatively large quantities. There appears in these cases to be a tendency for it to decrease as the frequency increases. It has not yet been discovered whether this is due to some effect inherent in the detailed mechanism of diffusion plus electrode process, or whether it is an artefact of some sort. In any case since rate of diffusion must tend to a limiting



100
400
R_r
50
350
$\frac{1}{\omega C_r}$
ohms
0
R_r
$\frac{1}{\omega C_r}$
5
$\frac{1}{\sqrt{\omega}} \times 10^2$
10 sec $\frac{1}{2}$
100
50
150
R_r
$\frac{1}{\omega C_r}$
ohms
300
200
100
R_r and $\frac{1}{\omega C_r}$ ohms

FIG 4.



200
100
ohms
2 5
$\frac{1}{\sqrt{\omega}} \times 10^2$
5
sec $\frac{1}{2}$
10

FIG. 5.

value for very high concentration gradients such as exist close to the electrode surface when the electrode process is very rapid, it is not certain how much of the rate control represented by $R_r - \frac{1}{\omega C_r}$ may be due to this cause. Thus for such cases as thallium, cadmium, lead (similar to cadmium) the constant can at present only be regarded as a lower limit for the true rate constant of the electrode process.

Rate constants for zinc as the hydrated ion and in complexes with bromide and iodide ions are given in Fig. (4). Those for zinc in M. KCl and KCNS are 6×10^{-3} and $1{\cdot}7 \times 10^{-2}$. Thus k increases in the order $k(NO_3^-) < k(Cl^-) < k(Br^-) < k(CNS^-) < k(I^-)$. Preliminary results for nickel and cobalt indicate a similar order for $k(Br^-)$, $k(CNS^-)$ and $k(I^-)$; these reactions are a great deal slower than for zinc. It appears possible that increasing covalency of bonding between the metal ion and its addenda, lowers the activation energy for discharge.

The addition of small amounts of surface active substances, such as gelatin or methyl red, to the solution has an interesting effect on the rates of rapid reactions. A very small amount has no effect, but as the amount is increased there is a sudden increase in R_r for the reaction, but little or no effect on $1/\omega C_r$. This implies a slowing down of some process at the electrode surface or very close to it, but not of the general rate of diffusion. With further increase in the concentration of the colloid, there is no further change in the reaction rate until there occurs another sudden decrease and the reaction becomes too slow for accurate measurement. These results are indicated in the graph of log k for M./2000 Cd^{++} in M. KNO_3 solution, against concentration of gelatin, Fig. 6. Further investigation of this effect is in progress.

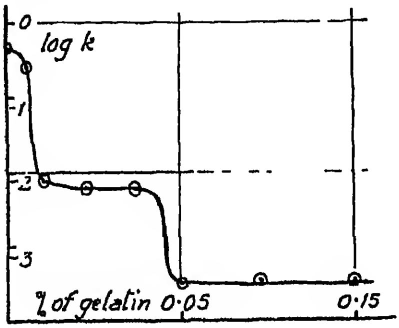


FIG. 6.

Appendix.

A.C. Conductance of a Dropping Mercury Electrode, at which a Reduction Process is Occurring.

A note on this subject is worth while in view of a recent publication [5] on the topic. At a mercury electrode at which a reduction process is occurring, both the reactant and product are present at the interface. When the current passing is equal to half the limiting diffusion current, the concentrations of the two are nearly equal if their diffusion coefficients are similar. The electrode therefore behaves similarly to the amalgam electrode described, except that its mean potential is not the equilibrium potential, but this difference is small for a rapid reaction. Starting from expression (10) it can be shown that the A.C. conductance of the electrode is a maximum when $C_1 = C_2$, i.e. for the dropping mercury electrode, when the D.C. component is half the limiting diffusion current. This is the result obtained by the authors of the paper cited, but their theoretical deduction of an expression in agreement with this, from the equation for the ordinary polarographic current-voltage curve, appears to the present author to be quite erroneous. That equation refers to what is, in effect, a steady state of the diffusion layer, and is not applicable to the alternating current process.

Summary.

A theoretical investigation has been made of the current passed by an electrode at which an electrochemical reaction is in equilibrium, when

[5] Breyer and Gutmann, *Trans. Faraday Soc.*, 1946, 42, 645.

it is subjected to a small alternating potential relative to the solution. Consideration of the electrode process, and diffusion, shows that the reaction is equivalent, electrically, to a capacity and resistance in series. Measurement of these quantities enables the rate constant for the electrode reaction to be calculated. Experiments have been carried out using a dropping amalgam electrode and results are presented in support of the theoretical equations. Rate constants for the discharge of a few metal ions are compared. Evidence has been obtained of a marked slowing down of rapid electrode reactions by the addition of surface active colloids to the aqueous solution.

Résumé.

On a fait l'étude du courant qui passe par une électrode, siège d'une réaction électrochimique en équilibre, lorsque la solution est soumise à de faibles potentiels alternatifs. Diverses considérations sur le processus à l'électrode et la diffusion montrent que la réaction est électriquement équivallente à une capacité et une résistance en série. La mesure de ces quantités permet de calculer la constante de vitesse. Des expériences, qui employaient une électrode à goutte d'amalgame, ont apporté des résultats, qui viennent appuyer les équations théoriques. Les constantes de vitesse pour la décharge de quelques ions métalliques sont comparées. On a mis en évidence un ralentissement marqué des réactions rapides à l'électrode par addition, à la solution aqueuse, de colloïdes actifs sur les surfaces.

Zusammenfassung.

Es wurde eine theoretische Untersuchung des Stromdurchgangs durch eine Elektrode, an der ein elektrochemischer Vorgang im Gleichgewichtszustand ist, wenn dieser im Verhältnis zur Lösung eine kleine Wechselspannung versetzt wird, durchgeführt. Eine Erwägung des Elektrodenprozesses und der Diffusion ergibt, dass—in elektrischer Beziehung—die Reaktion einer Kapazität und einem Widerstand in Hintereinanderschaltung äquivalent ist. Durch Messung dieser Grössen kann die Geschwindigkeitskonstante der Reaktion an der Elektrode berechnet werden. Es werden mit Benützung einer Amalgamtropfelektrode erhaltene Versuchsergebnisse angeführt, welche die theoretischen Gleichungen unterstützen. Die Geschwindigkeitskonstanten für die Abscheidung von einigen Metallionen werden verglichen. Beobachtungen weisen darauf hin, dass die Beifügung von oberflächenaktiven Kolloiden zu einer wässerigen Lösung rasche Elektrodenreaktionen merklich verzögert.

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THE BEHAVIOUR OF REVERSIBLE ELECTRODES IN ALTERNATING FIELDS.

BY B. BREYER AND F. GUTMANN.

Received 7th February, 1947.

It is the purpose of this communication to fill a gap in our knowledge of the mechanism of electrode processes, i.e. to provide a theory of the reversible depolarising process in the presence of a superimposed alternating field.

The following treatment applies to an electrode, which by increasing the applied direct potential passes from polarisation through a reversible stage into a state of concentration-polarisation, while at the same time a

small alternating voltage is superimposed on to the direct potential governing the electrode process. The electrochemical process is considered in the presence of a supporting electrolyte and the frequency of the alternating component is assumed to be small, i.e. of power-frequencies, compared with the relaxation time of the process.

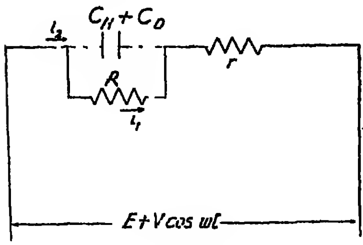

FIG. 1.

Such an electrode-system can be represented electrically by the network shown in Fig. 1.

r represents the total series resistance of the cell (including any polarisation resistance present) and C_H stands for the capacity of the Helmholtz-Gouy electric double layer. These two quantities remain constant throughout the reversible electrode reaction. R_D is termed the *dynamic resistance* and C_D the *dynamic capacitance*,[1] of the electrode system.

It will be shown that the magnitude of both is determined by the equilibrium-point of the electrode reaction.

At potentials higher than the decomposition voltage the electrode obeys

$$e = E_0 + \frac{RT}{nF}\log_e \frac{i_d - i}{i}, \quad . \quad . \quad . \quad . \quad (1)$$

which is Nernst's equation, expressed in terms of currents: i_d is the diffusion current, i stands for the current corresponding to an applied potential e, E_0 is the standard potential of the electrode process, and RT/nF has the usual meaning. By virtue of the superposition of a small alternating voltage $V \cos \omega t$ upon the applied direct potential E, the total instantaneous potential impressed is given by

$$e = E + V \cos \omega t. \quad . \quad (2)$$

Since equation (1) is non-linear, the resistance of the system will depend on the applied voltage. For direct currents an equivalent resistance is defined as the ratio e/i, but the alternating current resistance will differ from it, since the instantaneous potential given by (2) will periodically shift along the curve representing (1). This can be clearly seen from Fig. 2.

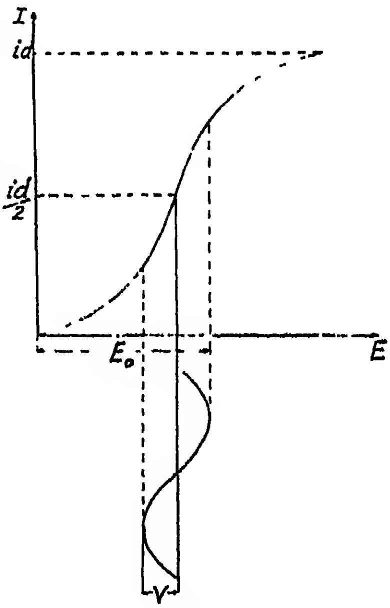

FIG. 2.

The network equations for Fig. 1 lead to a non-linear and non-homo-

[1] In a paper (*J. Amer. Chem. Soc.*, 1941, 63, 1207), Graham studied several kinds of capacitance which may be encountered in a study of the properties of the double layer by using a similar experimental arrangement as described by the present authors. When investigating the reversible electro-reduction Graham observed " phenomena which simulate the behaviour of a condenser of very large capacity ", and which he termed " pseudo-capacity ". This enters Graham's work only incidentally, while the present authors have devoted themselves to the theoretical treatment and computation of this capacitance.

geneous differential equation which cannot be solved in a closed and readily usable form. But inspection of Fig. 1 shows that the variations in the total cell-current are governed only by R_D and C_D, because r and C_H are constants.

The dynamic resistance R_D for any value of e is defined as the derivative of (1) evaluated at that point. Whence:

$$R_D = de/di = -\frac{RT}{nF} \cdot \frac{i_d}{i(i_d - i)} \cdot \qquad (3)$$

Equating $d(R_D)/di$ to zero yields a minimum of R_D at $i = \frac{i_d}{2}$, or, in terms of potentials, at $e = E_0$, i.e. at the standard potential of the electrode. The magnitude of R_D at this point is given by (4):

$$R_D = \frac{4RT}{nFi_d}. \qquad (4)$$

The minus sign in equation (3) merely indicates that a cathode is being considered and has been dropped in equation (4).

In order to predict the total alternating current passing through the cell, it is necessary to derive a quantitative expression for the dynamic capacitance C_D in terms of the instantaneous applied potential e.

While the static (or geometric) capacitance of a system of charged conductors is given by $C = Q/E$, for the present case of a non-linear relationship governing voltage and current the "dynamic capacitance" is defined by

$$C_D = dQ/de, \qquad (5)$$

i.e. by the rate of change of charge with the total impressed potential (direct and alternating). Since $i = dQ/d\zeta$, it follows from (2) and (5) that

$$1/C_D = dE/dQ - \frac{\omega V \sin \omega\zeta}{i}. \qquad (6)$$

Solving equation (1) for i and substituting into (6) yields:

$$1/C_D = dE/dQ - \frac{\omega V \sin \omega\zeta}{i_d} \cdot e^{(E + V \cos \omega\zeta - E_0)nF/RT}. \qquad (7)$$

dE/dQ represents the rate of change of charge with the applied direct potential. The electrode equation (1) can be expressed in terms of concentrations:

$$e = E_0 + \frac{RT}{nF} \log_e \frac{C^{el}_{ox}}{C^{el}_{red}}, \qquad (8)$$

where C^{el}_{ox} and C^{el}_{red} stand for the concentrations of the oxidised and of the reduced component respectively *at the electrode*. The net free charge residing within a space of small thickness d around an electrode of total area s is given by

$$Q_F = nFsd\,(C^{el}_{ox} - C^{el}_{red}). \qquad (9)$$

Assuming a linear concentration gradient and remembering that the current i transported by the ions is given by

$$i = nFsD\, dC/dx, \qquad (10)$$

where D = the diffusion coefficient, C the concentration at a point distant x from the electrode, it follows from (8) that

$$C^{el}_{ox} = C_{ox} - \frac{xi_d}{(1 + e^{(e - E_0)nF/RT}) \cdot DnF \cdot s}. \qquad (11)$$

The thickness of the diffusion layer x is related to i_d by

$$x = \frac{DnFs}{i_d} C_{ox}. \qquad \qquad (12)$$

Since the dropping mercury electrode offers the most practicable means of testing the validity of the present theory experimentally, i_d is expressed in terms of the Ilković Equation and s in terms of the capillary characteristics, viz., the mass of Hg flowing per second from the capillary (m) and the dropping time (t).

Combining (9), (11) and (12):

$$Q_t = \frac{0{\cdot}85\, nFd\, m^{\frac{2}{3}}\, t^{\frac{7}{6}} \left(e^{(e - E_0)nF/RT} - 1\right)}{e^{(e - E_0)nF/RT} + 1} C_{ox}. \qquad \qquad (13)$$

Differentiating (13), substituting the result and also the Ilkovič Equation for i_d into (7) and rearranging yields

$$C_D = \frac{e^{(E - E_0 + V \cos \omega\zeta)nF/RT}}{e^{(E - E_0 + V \cos \omega\zeta)nF/RT} + 1} \cdot \frac{1{\cdot}245\, (mt)^{\frac{2}{3}}\, dnFD^{\frac{1}{2}}\, C_{ox}}{\left(e^{(E - E_0 + V \cos \omega\zeta)nF/RT} + 1\right)\frac{RT}{nF} D^{\frac{1}{2}} 3{\cdot}4\, dt^{\frac{1}{6}} \omega V \sin \omega\zeta}. \qquad (14)$$

Differentiation of (14) shows that C_D has a maximum for all capillaries and for every ion species only and if

$$E + V \cos \omega\zeta = E_0. \qquad \qquad (15)$$

Since the amplitude of the superimposed alternating voltage is assumed to be small compared with the impressed direct potential, it follows that the dynamic capacitance attains its maximum at the standard potential E_0, when its instantaneous value is given by

$$C_D(E_0) = \frac{2{\cdot}49 (mt)^{\frac{2}{3}}\, dnFD^{\frac{1}{2}}}{4\frac{RT}{nF} D^{\frac{1}{2}} - 6{\cdot}8\, t^{\frac{1}{6}}\, d\omega V \sin \omega\zeta} C_{ox}. \qquad \qquad (16)$$

C_D thus oscillates around a mean value.

At E_0 and at the instant when $\sin \omega\zeta = \pm 1$,

$$C_D(E_0) = \frac{3{\cdot}66\, nF (mt)^{\frac{2}{3}}\, dD^{\frac{1}{2}}}{\left(8{\cdot}62\, D^{\frac{1}{2}}\frac{RT}{nF} + \omega V dt^{\frac{1}{6}}\right)} C_{ox}. \qquad \qquad (17)$$

Equation (17) gives the maximum value of the dynamic capacitance as registered by an instrument reading peak values of alternating current.

Since the dynamic resistance attains a minimum at the s.p. and the dynamic capacitance reaches a maximum at this point, a plot of the alternating current through the electrolysis cell against applied direct potential should show current maxima at the values of E_0 for the particular ion species undergoing discharge.

This conclusion has been tested experimentally on a number of ion species and Fig. 3 shows the curves obtained for a solution containing Cd^{++} and Zn^{++} ions.

The preceding reasoning need not be confined to ions but also applies to organic compounds which are capable of undergoing a reversible electro-reduction or -oxidation. 1-amino phenazine, for instance, gives a good A.C. maximum at the standard potential.

Both the dynamic capacitance and the dynamic resistance are proportional to the concentration and equations (4) and (17) permit the theoretical prediction of the alternating current passing through the system for a known concentration of a given ion. This has been tested in a number of ion species, covering a wide range of concentrations. A few

of the results obtained are listed in Table I. Fig. 4 shows the circuit which has been used for these determinations.

The series resistance r and the capacity of the Helmholtz-Gouy double layer C_H are responsible for the non-linearity between the alternating current and the concentration.

For numerical evaluations it is convenient to transform the circuit shown in Fig. 1 into a pure series circuit, as depicted in Fig. 5, employing the proper transformation-equations.

The quantity d appearing in the equations of the dynamic capacitance designates the thickness of that space within which a net free charge Q_f resides. Since the bulk of the solution is uncharged, d measures the thickness of that space around the electrode, in which an ionic space charge cloud is assumed to exist and within which the electrochemical process takes place. The magnitude of d depends on the nature of the supporting electrolyte present and varies with the nature of the ion species undergoing discharge. It is independent of the capillary characteristics but seems to be connected with the diffusion-coefficient of the ions. For Cd a value of 72 A. was found for d and for Tl, 216 A.

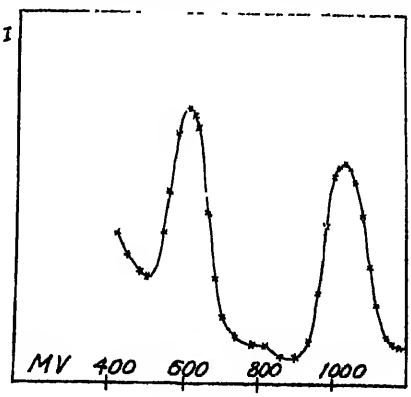

Fig. 3.

The mechanisms of transport of the direct and of the alternating current are quite different. While the direct current passing through the cell is due exclusively to the transport of electric charges by the ions across the electric double layer and their discharge at the electrode, the greater part of the alternating component is due to charge *transfers*. These transfers may or may not involve the actual discharge of the ions. They are characterised by changes in the instantaneous electrical state and spatial composition of the ionic atmosphere surrounding the electrode. The current component flowing by virtue of the dynamic capacitance represents an essentially reversible process and is due to changes in the energy stored in and released from the electric field between the ions during subsequent half-cycles. Since at every instant there exists an equilibrium between the oxidised and the reduced components in the proximity of a reversibly depolarised electrode, the relative concentrations of these two components will depend on the instantaneous potential. The resulting changes in the ion-atmosphere participating in the electrochemical reaction lead to changes in the electric field stored between the ions themselves and appear as the dynamic capacitance. It differs from

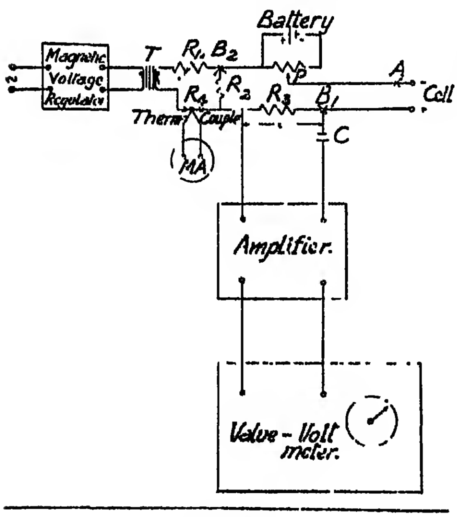

Fig. 4.

the capacitance of an ordinary, "geometric" condenser in some important aspects. The capacitance of the latter is a property of its geometric configuration, i.e. it is the consequence of the existence of a system of conductors separated by a dielectric. It has a certain capacity whether charged or not. The dynamic capacitance, on the other hand, appears only by virtue of the discharge process and without it ceases to exist.

At potentials below the discharge potential of a particular ion species, the dynamic capacitance is zero due to the absence of an electrochemical

TABLE I

t sec.	Compound.	Concentration. (M.)	Supporting Electrolyte. (N.)	$I\mu A$.	
				Calculated.	Observed.
2·06	$CdCl_2$	1/500	1/10 KCl	15·75	16·0
2·06	,,	1/20,000	,,	8·5	8·9
4·03	,,	1/500	,,	22·5	22·4
3·96	,,	1/1,000	,,	21·15	21·0
4·4	,,	1/2,000	,,	19·25	19·6
4·5	,,	1/4,000	,,	16·5	18·0
6·57	,,	1/8,000	,,	15·5	16·0
4·5	,,	1/20,000	,,	11·2	11·15
3·9	$TlNO_3$	1/500	1/10 KNO_3	22·0	21·8
4·1	,,	1/1,000	,,	18·3	18·0
4·2	,,	1/2,000	,,	16·3	16·4
4·2	,,	1/8,000	,,	12·9	13·4
4·3	,,	1/20,000	,,	11·4	11·9
3·4	$ZnSO_4$	1/1,000	1/10 KCl	16·95	15·75

process. Once the region of the diffusion current has been reached the oxidised component virtually disappears from the ionic atmosphere surrounding the electrode and C_D vanishes again at these corresponding potentials. The dynamic capacitance becomes a maximum at the standard potential, when the rate of change of the reaction, and therefore the transfer of electric charges, is a maximum.

The dynamic resistance, on the other hand, is due to the irreversible expenditure of energy during the discharge process. Consider a cathode at an instant when e has its peak value. From the total number of ions surrounding the electrode a certain number, governed by the Boltzmann-Maxwell distribution function for that particular energy, will be able to surmount the potential barrier at the surface of the electrode and will be discharged. A short time later the ion which, by diffusion, has taken the place of the discharged ion in the ordered structure of the ionic atmosphere, will possess a reduced energy resulting in a decreased probability of discharge. Simultaneously, the probability of an ion leaving the electrode and going over into the ionic atmosphere will increase. This is equivalent to saying that the ion which has previously been discharged again passes into solution. This cyclical process cannot occur without an increase in entropy of the system. Energy is expended and this gives rise to the dynamic resistance.

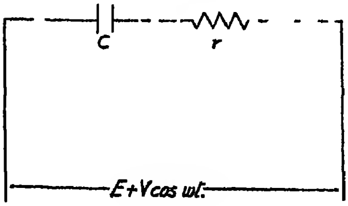

FIG. 5.

Physically, dynamic resistance and dynamic capacitance are due to the same electrochemical process, the distinction being that the one is due to the irreversible and the latter to the reversible part of the reaction.

In an ideal, perfectly reversible reaction there appears no dynamic resistance, but the dynamic capacitance would still be measurable. On the other hand, in an irreversible reaction the fundamental electrode equation (1) does not hold and no periodically varying equilibrium exists in the ionic atmosphere. Consequently, neither dynamic resistance nor dynamic capacitance can then exist and no significant changes in the superimposed alternating current can be expected.

This has been found to be the case. Compounds which are irreversibly reduced do not give rise to current maxima under the experimental conditions as used by the present authors. The presence of oxygen, e.g. does not give rise to any significant changes in the alternating current.

A further storage of electrical energy occurs between the ionic space charge as a whole and the electrode. This gives rise to the capacitance of the electric double layer; it is discharge independent and is primarily governed by the supporting electrolyte. The latter, as far as is known, also determines the thickness of the double layer itself. This is quite distinct from the thickness of the ionic space charge actually participating in the electrochemical reaction, and which is measured by the quantity α in the equations of the dynamic capacitance.

The present experimental method is also very suitable for the measurement of the capacity of the electric double layer and determinations of the electrocapillary zero point. An alternating current minimum can be observed at this point. As an example of this, the authors observed the electrocapillary zero of 10^{-3} N. HCl at -470 mv. against S.C.E. Measuring the cell impedance at the electrocapillary zero point (by inserting a known resistance in series with the cell, sufficient to halve the original current reading), permits the capacity of the double layer to be evaluated. The authors found for mercury a value of 5·75 μF./cm.^{2}, which is in good agreement with the values calculated by Vorsina and Frumkin[8] from Stern's theory.

Résumé.

On établit une théorie du processus réversible dépolarisant, qui a lieu en présence d'un champs alternatif surimposé, dont les fréquences sont petites comparées avec le temps de relaxation du processus électrochimique et on donne le calcul de la capacité et de la résistance dynamiques. On montre que les courbes du courant alternatif à travers la cellule, en fonction du potentiel direct appliqué, présentent des maxima à partir desquels on peut estimer les valeurs du potentiel standard du processus à l'électrode. La méthode peut être étendue à des composés organiques, capables de subir une électro-réduction ou oxydation. On décrit la méthode expérimentale, qui utilise une électrode à goutte de mercure, et ses emplois pour déterminer la capacité de la double couche électrique et le point zéro électrocapillaire.

Zusammenfassung.

Eine Theorie des reversibeln Depolarisationsvorganges, der in Gegenwart eines zusätzlichen wechselnden elektrischen Feldes—dessen Frequenzen im Verhältnis zur Relaxationszeit des elektrochemischen Vorgangs klein sind—stattfindet, wird ausgearbeitet und die dynamische Kapazität und der dynamische Widerstand berechnet. Es wird gezeigt, dass die Kurve für die Beziehung zwischen der Wechselstromstärke durch das Messgefäss und dem angewandten Gleichstrompotential Strommaxima aufweist, aus denen das Normalpotential des Elektrodenvorgangs gefunden werden kann. Die Methode kann auf organische Verbindungen, die elektrolytisch

[8] Vorsina and Frumkin, *Acta Physicochim.*, 1943, 18, 247.

reduzierbar oder oxydierbar sind, ausgedehnt werden. Die experimentelle Methode, die eine Quecksilbertropfelektrode verwendet, und Anwendungen auf Bestimmung der Kapazität der elektrischen Doppelschicht und des elektrocapillaren Nullpunkts werden beschrieben.

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DIFFUSION AND CONVECTION AT ELECTRODES.

By J. N. Agar.

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Movement of solute between the bulk of the liquid phase and the electrode/solution interface is an essential feature of all electrode reactions; dissolved reactants must be supplied to the interface or products must be removed. This movement can occur in three ways: (i) by diffusion; (ii) by convection (i.e. movement of the liquid containing the solute); (iii) by ionic migration. Migration and convection cannot account for the whole of the material required or produced by the reaction, and the co-operation of diffusion is always necessary; the concentrations at the interface must therefore differ from those in the bulk of the solution. Such concentration differences are responsible for concentration over potential[1] and limiting currents, and have an important influence on the kinetics of electrode reactions generally.

These effects are usually discussed in terms of the Nernst diffusion layer hypothesis (see next section), which can hardly be considered a satisfactory theoretical treatment of the subject. In this paper a different method is adopted; the variables involved in the problem are found by inspection of the fundamental equations and certain properties of the relations between these variables are then derived by dimensional analysis.[2] Further information can be obtained by considering experimental and theoretical results relating to the closely analogous subject of heat transfer.

It is necessary to restrict the discussion to systems in which the transport number, T_s, of the ion or molecule concerned is constant; in other cases, calculation of the effect of migration becomes too complicated. T_s is constant, or approximately constant, for:

(*a*) non-ionised solutes or ions in a large excess of some other electrolyte ($T_s = 0$; no migration);

(*b*) solutions containing only two ions (i.e. a single salt).

No more need be said about (*a*); in (*b*), migration is responsible for a definite fraction of the total transfer of solute, and the remainder is transferred by diffusion and convection, which proceed as if no migration were occurring.[1, 3] The transfer rate, j, defined below, always refers to this latter fraction, due to diffusion and convection and not to migration. The same transfer rate is thus relevant to non-electrolytic reactions at a solid/liquid interface.

It is sometimes possible to ensure that the liquid containing the electrode is stationary, so that there is no convection.[4] But the liquid is usually in motion, owing to (i) intentional stirring (forced convection),

[1] Agar and Bowden, *Proc. Roy. Soc. A*, 1938, **169**, 206.
[2] See Bridgman, *Dimensional Analysis* (Newhaven, 1931).
[3] Roseburgh and Lash Miller, *J. Physic. Chem.*, 1910, **14**, 816; see also Levich (ref.[11]).
[4] e.g. Sand, *Phil. Mag.*, 1901, **1**, 45.

(ii) gravitational motion due to variations in density associated with concentration changes (natural convection), (iii) evolution of gas at the electrode, (iv) temperature gradients within the cell, and (v) adventitious causes such as vibration. The present paper is concerned with (i) and (ii); (iii) may be regarded as an extreme case of (ii), but probably involves additional factors such as bubble size.

The complete calculation of the convective transfer depends on the solution of intractable hydrodynamical problems, but a partial solution can be obtained quite simply by dimensional analysis; this method has proved very useful in the treatment of thermal convection.[5] The close analogy between heat transfer and mass (solute) transfer has long been known, and has been widely used in the study of mass transfer in gases.[6] The possibility of extending the analogy and the use of dimensional methods to mass transfer at a solid/liquid interface has also been recognised,[7, 8, 9] but it does not seem that its implications have been fully considered.

It would, of course, be more satisfactory to obtain a complete solution of the equations of hydrodynamics and convective transfer. Several problems in thermal convection have been worked out in detail [10] mostly in terms of Prandtl's boundary layer theory and three important papers by Levich [11, 12, 13] deal with convection at an electrode in a similar manner. But all such solutions are at present limited to cases where the geometry of the cell and electrode is simple, and restrictions may also be imposed on the size of the electrode. In practice, the design of cells and electrodes is governed by factors other than geometrical simplicity, and electrochemical experiments are often carried out under conditions which, from the hydrodynamical point of view, are impossibly complicated.

The Nernst Diffusion Layer.

Nernst [14] postulated a stationary layer of liquid in contact with the electrode; within the layer only diffusion is operative, while outside the layer the concentration is maintained at a constant value, c_B, by convection, and diffusion is negligible. If the electrode is plane, the steady concentration gradient in the layer is linear and the rate at which a solute passes through it (the transfer rate) is:

$$j = \frac{D(c_s - c_B)}{\delta} \quad . \quad . \quad . \quad . \quad (1)$$

where D is the diffusion coefficient of the solute, c_B and c_s are respectively the concentrations in the bulk and at the electrode and δ is the thickness of the layer.

In practice, δ is calculated by the formula

$$\bar{j} = \frac{D(c_s - c_B)}{\delta} \quad . \quad . \quad . \quad . \quad (1a)$$

where $\bar{j}$ is the mean value of j over the whole electrode (mean transfer rate), and the same equation is used without modification for non planar electrodes.

[5] Rayleigh, *Nature*, 1915, **95**, 66. McAdams, *Heat Transmission* (McGraw-Hill, 1942). ten Bosch, *Wärmeübertragung* (Springer, 1936).
[6] e.g. Sherwood, *Absorption and Extraction* (McGraw-Hill, 1937).
[7] King and Howard, *Ind. Eng. Chem.*, 1937, **29**, 75.
[8] Hixson, *ibid.*, 1944, **36**, 488. Hixson and Baum, *ibid.*, 1941, **33**, 478; 1942, **34**, 120.
[9] Uchida, *J. Soc. Chem. Ind. Japan*, *B*, 1933, **36**, 416; 1934, **37**, 456. Uchida and Nakayama, *ibid.*, 1933, **36**, 635.
[10] See ten Bosch (ref.[5]) and Goldstein (ref.[18]), ch. 14.
[11] Levich, *Acta Physicochim.*, 1942, **17**, 257.
[12] Levich, *ibid.*, 1944, **19**, 117.
[13] Levich, *ibid.*, 1944, **19**, 133.
[14] Nernst, *Z. physik. Chem.*, 1904, **47**, 52.

Provided the transport number T_a is independent of concentration (including the case where migration is negligible and $T_a = 0$), $\bar{j}$ is given by:

$$j = \frac{I(1 - T_a)}{AzF}$$

where I is the total current, A the electrode area, F the Faraday, z the number of Faradays required per mole, reacting and T_a the transport number of the reacting ion.[c]

In reality the transition from diffusion alone at the electrode surface, to convection alone in the bulk must take place continuously; diffusion and convection will be equally important at some distance δ' from the surface, where δ' is of the same order as δ. Any factor which increases convection (e.g. increase of liquid velocity) will diminish δ'; an increase of the diffusion coefficient will enlarge the zone in which diffusion is predominant and will thus increase δ'. Similar changes in δ are to be expected.[15]

The experimental values of δ are around 0·05 cm. for vertical surfaces in unstirred solutions (natural convection) and 0·005 cm. or less in stirred solutions, according to the rate of stirring.[16] It thus appears that forced convection due to the ordinary laboratory methods of stirring is much greater than natural convection; the latter can therefore be neglected in stirred solutions, and the two types of convection can be considered separately.

The Equations of Diffusion and Convection.

The rate of change of concentration, c, at any point in the solution is given by the differential equation:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) - \left(u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z}\right) \quad . \quad (2)$$

or in vector notation (cf. Levich [11]):

$$\frac{\partial c}{\partial t} = D \operatorname{div} \operatorname{grad} c - \mathbf{v} \operatorname{grad} c \quad . \quad . \quad . \quad (2a)$$

where t is time, D is the diffusion coefficient, and u, v and w are the x, y and z components of the velocity $\mathbf{v}$ at the point x, y, z. The first term on the right represents the effect of diffusion, which is assumed to obey Fick's law as in a stationary liquid; the second term gives the change in concentration due to convection.

As the equation is linear in c, we can replace c by the concentration difference $\theta = c - c_0$; hence:

$$\frac{\partial \theta}{\partial t} = D \operatorname{div} \operatorname{grad} \theta - \mathbf{v} \operatorname{grad} \theta \quad . \quad . \quad . \quad (3)$$

At the electrode surface, u, v and w are zero and transfer is entirely by diffusion, so we have the two boundary conditions:

$$c = c_s \quad \text{or} \quad \theta = c_s - c_0 \quad . \quad . \quad . \quad . \quad (4)$$

and

$$j = -D\left(\frac{\partial c}{\partial n}\right)_{n=0} = -D\left(\frac{\partial \theta}{\partial n}\right)_{n=0} \quad . \quad . \quad . \quad (5)$$

where j has the same meaning as in (1) and n represents distance from the electrode measured normally to the surface.

[15] King, *J. Amer. Chem. Soc.*, 1935, **57**, 828.

[16] Nernst and Merriam, *Z. physik. Chem.*, 1905, **53**, 235. Brunner, *ibid.*, 1904, **47**, 56; and see the review of the subject by Glasstone and Hickling, *Electrolytic Oxidation and Reduction* (Chapman and Hall, 1935).

It will be assumed that c has the same value at all points on the electrode. This is always true under limiting current conditions, when ... over the whole electrode surface, but it is not necessarily true in other cases. For a highly reversible reaction, c will be related to the metal-solution potential difference by the usual Nernst equation, but this will vary from point to point to an extent determined by the distribution of current and the specific resistance of the electrolyte. The variation of E and ... is probably negligible for relatively small electrodes in electrolyte of high conductivity.[17] Further complication arises if the electrode reaction is irreversible.

The experimentally important mean transfer rate j is given by

$$j = \frac{1}{A}\int^{A} j \, dA$$

where A is the area of the electrode.

The Equations of Motion.

The following brief discussion is given in order to show the factors on which the motion depends. Full accounts are, of course, to be found in standard works on hydrodynamics.[18]

The components of velocity, u, v, w, in a liquid are determined by the equation of continuity

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$$

together with the three Navier-Stokes equations

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z} = -\frac{1}{\rho}\frac{\partial P}{\partial x} + X + \nu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) \qquad (6)$$

and two analogous equations in v and w. ρ, P and ν are respectively the density, total pressure and kinematic viscosity (i.e. viscosity/density), and X is the x component of the extraneous forces acting on unit mass of the liquid. The terms on the left taken together are the acceleration of a particle of the liquid, and after multiplying by ρ (6) has the form

density × acceleration = pressure gradient + extraneous force + viscous force

The extraneous force to be considered is gravity, and in a liquid of constant density it is balanced by the hydrostatic pressure P_0, so that X may be omitted if P is replaced by $p = P - P_0$. But if the density is variable the effect of gravity cannot in general be balanced by a hydrostatic pressure, and the equation becomes

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \frac{g(\rho - \rho_0)}{\rho} + \nu\nabla^2 u \qquad (7)$$

where g is the acceleration of gravity and $g(\rho - \rho_0)$ is the excess force resulting from variation in ρ, the x axis being supposed vertical.

In the present case, the variation in density arises from variation in concentration, and if only one solute is concerned, we may put

$$\frac{\rho - \rho_0}{\rho} = \alpha(c - c_0) = \gamma\theta \qquad (8)$$

where ρ_0 is the density at concentration c_0. The density coefficient α determines the change of density with concentration and is assumed

[17] Hoar and Agar (in course of publication).

[18] Goldstein, *Modern Developments in Fluid Dynamics* (Oxford 1938); Lamb, *Hydrodynamics* (Cambridge 1932).

to be constant. $\rho - \rho_0$ will usually be small compared to ρ_0, and (7) thus becomes approximately:

$$\frac{\partial u}{\partial t} = u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z} = -\frac{1}{\rho_0}\frac{\partial p}{\partial x} + g\alpha\theta + \nu\nabla^2 u. \quad . \quad (9)$$

As already stated, the effect of natural convection (i.e. of gravitational motion) is negligible under forced convection conditions, and the $g\alpha\theta$ term may then be omitted.

Although pressure gradients and velocities appear in the equations of motion, pressure and velocity cannot both be taken as independent variables. It is usually most convenient to choose velocity as an independent variable; p is then, in principle, determined by the equations, and no further consideration need be given to it, nor to quantities such as ρ_0 which appear only in conjunction with p.

In forced convection problems, some characteristic velocity U (e.g. peripheral speed of a stirrer; mean rate of flow through a tube) must be specified. In natural convection, U may be put equal to zero (stirrer stationary), and therefore does not appear as a variable. In addition, the time, t, may be omitted from any relation that refers to a steady state of diffusion and convection. It is worth noting, however, that in turbulent motion the velocities fluctuate about a mean value, and similar fluctuations must occur in c, j, etc. Experimentally, the important quantities are the average values over a long period, and they will be independent of t.

Application of Dimensional Analysis.

(1) Forced Convection.—The solution of the differential equations is a function of the coefficients which occur in them and of the quantities appearing in the boundary conditions. Hence $\bar{j}$ depends on U, ν, D and $(c_s - c_0)$; it also depends on the distance n appearing in (5) and on the various spatial co-ordinates which determine the position and size of the electrode (including its area A), and of the other boundary surfaces. All these latter quantities can be expressed in terms of some characteristic length l (e.g. the length of the electrode), together with dimensionless ratios of the type x/l. The problem thus involves six dimensional quantities, $\bar{j}$, U, ν, l, D and $(c_s - c_0)$.

It must be possible to express the relation between these six quantities in a form which is independent of the units employed, i.e. as a relation between dimensionless groups.[3] Table I shows the dimensions and units

TABLE I.

Symbol.	Transfer of Solute.		Transfer of Heat.
	Quantity.	Dimensions.	Quantity.
$\bar{j}$	Mean transfer rate (moles./cm.^{2} sec.)	$ML^{-2}T^{-1}$	Mean transfer rate (cal./cm.^{2} sec.)
$c_s - c_0 = \theta$	Concentration difference (moles./cm.^{3})	ML^{-3}	(Temp. difference) $\times S$ (cal./cm.^{3})
D	Diffusion coefficient (cm.^{2}/sec.)	L^2T^{-1}	Thermal diffusivity (cm.^{2}/sec.)
ν	Kinematic viscosity (cm.^{2}/sec.)	L^2T^{-1}	(As for solute)
l	Characteristic length (cm.)	L	(As for solute)
U	Characteristic velocity (cm./sec.)	LT^{-1}	(As for solute)
$(g\alpha)$	Gravity $\times$ density coefft. (cm./sec.^{2}) $\times$ (cm^3/mole.)	$M^{-1}L^4T^{-2}$	(Gravity $\times$ thermal expansion coefft.)/S

S = specific heat per unit volume.

of $\bar{j}$, U, ν, l, D and $(c_s - c_0)$, and the analogous variables which occur in heat transfer problems.

Elimination of the three fundamental units M, L and T imposes three conditions; hence $6 - 3 = 3$ independent dimensionless quantities can be formed from the six variables. They may be chosen in various ways, but the following are most convenient:

Reynold's number: $Re = \dfrac{Ul}{\nu}$

Nusselt's number: $Nu = \dfrac{\bar{j}l}{\Theta D}$

Prandtl's number: $Pr = \dfrac{\nu}{D}$

where $\Theta = (c_s - c_0)$.

The nomenclature follows the usage of hydrodynamics and heat transfer; the nature of the corresponding thermal quantities will be clear from Table I. The relation between the six variables can thus be reduced to:

$$Nu = \mathrm{F}(Re, Pr) \quad . \quad . \quad . \quad . \quad (10)$$

The form of the function F depends only on the shape of the apparatus.

(2) Natural Convection.—The characteristic velocity U does not appear in natural convection problems, but the quantities g and α have to be included. They need not be considered separately, since only their product $(g\alpha)$ occurs in the equations (see (9)); the dimensions of $(g\alpha)$ are given in Table I. From the six variables $\bar{j}$, l, ν, D, Θ and $(g\alpha)$, three dimensionless quantities can be formed; the usual choice is Nu and Pr as in forced convection, together with:

Grashof's number: $Gr = \dfrac{l^3 g\alpha\Theta}{\nu^2}$.

We thus have:

$$Nu = \mathrm{G}(Gr, Pr) \quad . \quad . \quad . \quad . \quad (11)$$

where the form of the function G depends only on the shape of the apparatus.

Under certain conditions this equation can be simplified.[19] If the velocity of motion is small and steady, the acceleration of any element of the fluid (i.e. the left hand side of (9)) becomes negligible; the pressure gradient and gravity are balanced by viscous forces alone. (9) can now be rewritten so that ν appears only in the pressure terms, which are of no further interest, and in a coefficient $(g\alpha)/\nu$; in the final solution ν must therefore occur only in this form. This condition is satisfied by introducing Gr and Pr into the function G as their product $Gr \, . \, Pr$, so that:

$$Nu = \mathrm{G}(Gr, Pr) = \mathrm{G}'(Gr \, . \, Pr) = \mathrm{G}'\left(\frac{l^3 g\alpha\Theta}{\nu D}\right) \quad . \quad . \quad (12)$$

Heat transfer measurements show that the simplified equation holds over a wide range of Gr and Pr.[20]

The discussion has so far been restricted to reactions where only one solute is concerned (e.g. deposition of Cu from $CuSO_4$ solution). Many electrode reactions, and other surface reactions, are more complicated, since the density of the solution depends on the concentration of two or more solutes. Examples are:

(i) reactions in which reactants and products are both in solution, e.g. $Fe^{+++} + e^- \rightarrow Fe^{++}$;

(ii) deposition of, e.g., a metal from excess of indifferent electrolyte; there are changes in the concentrations of metal ion and of indifferent electrolyte.

[19] Davis, *Phil. Mag.*, 1922, 44, 926. [20] See McAdams (ref.[9]), p. 243.

Assuming that the changes in density due to the various solutes, numbered 1, 2, 3, etc., are additive, the term $g\alpha\theta$ in (9) must be replaced by $g(\alpha_1\theta_1 + \alpha_2\theta_2 + \ldots)$, and there must be equations similar to (3), (4) and (5) for each solute, involving its concentration and its diffusion coefficient (D_1, D_2, etc.). It does not seem possible to derive simple expressions analogous to (11) and (12), but approximate values of Nu will be given by

$$Nu_1 = Nu_2 = \ldots = \mathrm{G}'\left[\frac{l^3 g(\alpha_1\theta_1 + \alpha_2\theta_2 + \ldots)}{\nu D_m}\right] \quad . \quad (13)$$

where D_m is the arithmetic mean diffusion coefficient. The use of D_m can be justified on the grounds that the differences between the various D's are usually small and that the value of Nu is not very sensitive to changes in the variable $Gr \, . \, Pr$, as will appear later.

The effect of variations in density due to temperature gradients is probably small (see Levich [12]) and they have been neglected. Temperature gradients may arise from the Joule heating effect of the current and from the heat of reaction at the electrode. The former will certainly be negligible at small current densities; the latter may escape by conduction through the electrode or, in other types of apparatus, may be transferred to the solution, in which case " heat " may be treated as an additional solute.

Comparison with Experiment.

Equations (1*a*), (10), (11) and (12) show that the thickness of the Nernst diffusion layer is given by

$$\delta_f = \frac{l}{\mathrm{F}(Re, Pr)} \qquad \text{(forced convection)} \quad . \quad (14)$$

and

$$\delta_n = \frac{l}{\mathrm{G}(Gr, Pr)} \quad \text{or} \quad \frac{l}{\mathrm{G}'(Gr \, . \, Pr)} \qquad \text{(natural convection)} \quad . \quad (15)$$

where the subscripts f and n show the type of convection.

In forced convection, δ_f is independent of the concentration difference, $\theta = c_s - c_0$, since neither Re nor Pr depend on θ; in other words, j is proportional to $c_s - c_0$. This result is analogous to Newton's Law of Cooling in the thermal case. In natural convection, on the other hand, δ_n is a function of $Gr = l^3 g\alpha\theta/\nu^2$, and therefore varies with the concentration difference (or with the current density). It is obvious that there must be some such variation of δ_n, since the velocity of motion depends on the density difference. Both these conclusions are supported by experiment, although δ_n does not, in fact, vary much with the concentration difference and may often be considered constant.

Further information about the functions F, G and G′ has to be derived from experiment (including heat transfer measurements) or from the more complete theoretical solutions which have been obtained in certain simple cases.

Forced Convection.—Assuming that F can be expressed in the form:

$$\mathrm{F}(Re, Pr) = B \, . \, (Re)^a (Pr)^b \quad . \quad . \quad . \quad (16)$$

where B is a constant, we have:

$$\delta_f = \frac{l}{B} (Re)^{-a} (Pr)^{-b}.$$

The effect of stirring velocity, U, on δ_f, in electrode and other surface reactions, has been investigated by many authors, and the results have usually been found to obey a law of the form

$$\delta_f = \text{const.} \; U^{-m}$$

with values of m ranging from 0·5 to 1, according to the type of apparatus and stirring.[11] Comparison with (16) shows that $m = a$.

There is little direct information about the value of b, which determines the effect of Pr (i.e. of D), or about the influence of changes in ν and l. Hixson and Baum,[8] from the rate of solution of benzoic acid tablets in stirred liquids of various ν and in geometrically similar vessels of differing sizes, found $a \simeq 1$ and $b = 0{\cdot}5$; King and Howard [7] found $b = 0{\cdot}3$ from the rate of solution of metallic wires in various reagents, and $b = 0{\cdot}17$ on the basis of earlier experiments. King and Howard also measured heat transfer from electrically heated wires in the same apparatus and showed that it could be correlated with the mass transfer observations by an equation similar to (16).

The data derived from heat transfer measurements are much more complete. For turbulent flow through long pipes, McAdams [5] gives

$$Nu = 0{\cdot}023\ (Re)^{0.8}\ (Pr)^{0.1} \qquad . \quad . \quad . \quad (17)$$

using the mean velocity of flow (cc. per sec. per sq. cm. cross section) and the diameter as the characteristic velocity, U, and length, l. Similar equations have been proposed for transverse flow past wires and pipes. It should be possible to calculate diffusion layer thicknesses from equations such as (17) (cf. King and Howard [7]), and a rough calculation, using (17) for a tube 1 cm. in diameter with $U = 100$ cm. per sec. and values of ν and D given in Table II leads to $\delta_t \simeq 0{\cdot}002$ cm., which is of the order commonly observed, although there do not appear to be any recorded measurements of δ for flow through tubes. Uchida [9] has found, moreover, that the rate of attack of copper tubes by ammonia solution is proportional to the 0·79 power of the velocity of flow, and has drawn attention to the close agreement with the exponent 0·8 in (17). The rate of attack is probably controlled by the rate at which dissolved oxygen reaches the surface of the metal.

Laminar flow along a flat electrode has been treated theoretically by Levich,[11] and, with rather different approximations, by Eucken.[22] The general equation for convection in this case, if $Pr > 1$,* has the form : [23]

$$Nu = \text{const.}\ (Re)^{\frac{1}{2}}(Pr)^{\frac{1}{3}}.$$

Levich has also considered a rotating disc electrode; putting $D = 10^{-5}$ cm.^{2} sec.$^{-1}$ and $\nu = 10^{-2}$ cm.^{2} sec.$^{-1}$ (see Table II), he finds :

$$\delta = \frac{0{\cdot}022}{\sqrt{\text{rev. per sec.}}}\ \text{cm.}$$

Natural Convection.—A theoretical solution of the natural convection equations for heat loss from vertical plates in air has been obtained by Schmidt, Pohlhausen and Beckmann; [24] when reduced to the simplified form (12), it becomes :

$$Nu = G'\ (Gr\,.\,Pr) = 0{\cdot}525\ (Gr\,.\,Pr)^{\frac{1}{4}} = 0{\cdot}525\left(\frac{l^3 g\alpha\theta}{\nu D}\right)^{\frac{1}{4}} \quad . \quad (18)$$

and this equation should hold for other types of convection in other media. Nu is independent of the width of the plate provided it is large compared to δ, and the relevant characteristic length to be used in (18) is the height. A similar expression is given by Levich.[11]

Fig. 1 shows the theoretical relation between log Nu and log ($Gr\,.\,Pr$) according to (18), and also according to data derived from heat transfer measurements given by McAdams.[5] The two curves agree well from $Gr\,.\,Pr = 10^4$ to $Gr\,.\,Pr = 10^9$. If the diameter is used as the character-

* $Pr = \nu/D$ is of the order 10^3 for diffusion of electrolytes in aqueous solution at room temperature. See Table II.

[21] Glasstone and Hickling, ref.[16].

[22] Eucken, *Z. Elektrochem.*, 1932, 38, 341.

[23] See, e.g., Goldstein, ref.[18], ch. 14.

[24] See ten Bosch (ref.[5]), p. 159.

istic length l, the experimental heat transfer curve for long horizontal wires lies very close to that for vertical plates.

As already mentioned, the $Gr . Pr$ product for convection in electrode processes is often a rather complicated quantity. But in most cases the various θ's appearing in (13) are proportional to one another and roughly equal numerically; we can thus use the simpler expression (12) if α now

TABLE II.

	l cm.	$(g\alpha)$ cm.^{4}/sec.^{2} mole.	θ mole./cm.^{3}	ν.	D.	$(Gr . Pr)$.	Nu.	δ_n. cm.
				cm.^{2}/sec.				
(a)	1·0	40×10^3	10^{-5}	10^{-2}	10^{-5}	4×10^6	26·3	0·038
(b)	0·1	40×10^3	10^{-6}	10^{-2}	10^{-5}	4×10^2	3·24	0·031

represents a suitably chosen "overall" density coefficient. Table II shows the data used in two calculations of $Gr . Pr$, (a) for an electrode 1 cm. high with concentration difference 0·01 M.; (b) for an electrode 0·1 cm. high with concentration difference 0·001 M. α is taken to be 40 cm.^{3} mole.$^{-1}$, which is typical of salts such as KCl; α is larger for heavy metal salts, but the lower value has been used since the density is often determined by a differential effect—increase of concentration for one solute and decrease for another. ν and D are typical values for aqueous salt solutions at room temperature.

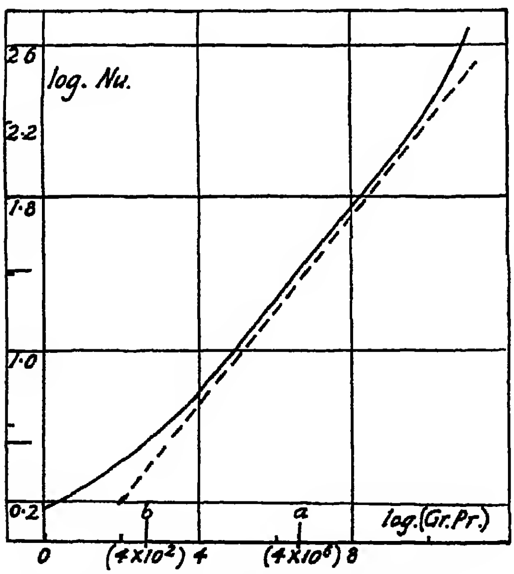

FIG. 1.—Natural convection for vertical plate.
– – – – – Theoretical (eqn. 18).
———— Experimental (McAdams) (heat transfer).

The values of $Nu = G'(Gr . Pr)$ corresponding to $Gr . Pr = 4 \times 10^{-2}$ and 4×10^{-6} are obtained from the *experimental* heat transfer curve, Fig. 1, and the thickness of the diffusion layer is calculated by (15). It will be seen that they agree reasonably well with the commonly observed value 0·05 cm.; when it is remembered that the calculation is based on heat transfer measurements, mainly for large plates in air, the agreement may be considered very satisfactory. It is clear from the graph that the theoretical equation (18) would give nearly the same δ at $Gr . Pr = 4 \times 10^{-6}$ but a somewhat larger value at $Gr . Pr = 4 \times 10^{-2}$.

From (15) and (18), it appears that:

$$\delta_n = \frac{l}{0{\cdot}525\left(\frac{l^3 g\alpha\theta}{\nu D}\right)^{\frac{1}{4}}} = 1{\cdot}91\left(\frac{l\nu D}{g\alpha}\right)^{\frac{1}{4}} . \theta^{-\frac{1}{4}} \qquad . \qquad . \quad (19)$$

so that δ_n should change appreciably with the concentration difference θ. It is often stated that δ_n is independent of θ, and this seems to be particularly well established for the stationary platinum wire "micro-electrodes" used by Laitinen and Kolthoff.[25] It is, however, to be expected that δ_n will be relatively insensitive to changes in θ when very small electrodes are used; there are two reasons:

(i) if the linear dimensions in all three directions of the electrode are small, the mass transfer due to diffusion alone (without convection) becomes appreciable; for transfer of this type, δ is constant;

(ii) the experimental heat transfer curves for *wide* plates and *long* wires (Fig. 1), where (i) is of no importance, flatten out at low values of $Gr \, . \, Pr$, i.e. the exponent in (18) becomes less than $\frac{1}{4}$. Since $Gr \, . \, Pr$ diminishes rapidly with the linear dimensions, a similar effect may occur with Laitinen and Kolthoff's short wire micro-electrodes.

As regards larger electrodes, some of the available data[26] show a definite trend of δ_n in the expected direction, although it is not as large as predicted by (19). Further evidence on this point is given in the following section.

Concentration Overpotential under Natural Convection Conditions.

The variation of δ_n with θ which is to be expected under natural convection conditions, has an effect on the relation between current and concentration overpotential. Assuming that all the variables except j, θ and δ_n remain constant, and that

$$Nu = (Gr)^n \, . \, f(Pr) \qquad \text{(cf. (11))}$$

we have

$$\delta_n = k_1\theta^{-n} \qquad \text{(cf. (19))}$$

and

$$I = k_2 j = k_3\theta^{n+1}$$

where I is the total current and k_1, k_2 and k_3 are constants.* Assuming further that the potential of the electrode is controlled by the concentration of only one solute and that diffusion potentials can be neglected, the concentration overpotential,[1] η_c, is given by:

$$\eta_c = \frac{RT}{zF}\ln\frac{c_e}{c_0} = \frac{RT}{zF}\ln\left(1 \pm \frac{\theta}{c_0}\right) = \frac{RT}{zF}\ln\left[1 \pm \left(\frac{I}{I_0}\right)^{\frac{1}{n+1}}\right] \qquad (20)$$

where $I_0 = k_3 c_0^{n+1}$. The positive sign is to be used when $c_e > c_0$; the negative when $c_e < c_0$.

When $c_e \gg c_0$, (20) becomes[1]

$$\eta_c = \frac{1}{n+1} \cdot \frac{RT}{zF}\ln\frac{I}{I_0} \quad \text{or} \quad V_e = V_0 + \frac{1}{n+1} \cdot \frac{RT}{zF}\ln I \quad . \quad (21)$$

if V_e is the potential measured against a standard reference electrode. n can thus be determined from the slope of the potential — log (current) curves.

With this object, some observations have been made on the deposition of iodine from KI solutions, at flat vertical platinum anodes 1·0 to 2·9 cm. high and 1·0 cm. wide, in unstirred solutions at 21° C. Brunner[27] has shown that iodine is liberated without any measurable activation overpotential, and the potential is thus controlled by the concentration of

* θ, I and I_0 are to be taken as positive quantities, irrespective of their true sign.

[25] Laitinen and Kolthoff, *J. Physic. Chem.*, 1941, **45**, 1061.

[26] e.g. Wilson and Youtz, *Ind. Eng. Chem.*, 1923, **15**, 603. Collenberg and Bodforss, *Z. physik. Chem.*, 1922, **101**, 117.

[27] Brunner, *Z. physik. Chem.*, 1907, **58**, 1.

I_3^- in contact with the electrode. The concentration of KI was N. or 5 N., and the effect of changes in $[I^-]$ is negligible; the concentration of I_3^- in the bulk, i.e. c_0, was zero. Under these conditions (21) should hold, and, introducing the appropriate values of z, etc., it becomes

$$V_e = V_0 + \frac{0 \cdot 029}{n + 1} \quad \log_{10} I$$

in volts. Measurements of the potential of the anode (against saturated calomel) at various currents showed that the relation between V_e and $\log I$ was linear; the observed slopes ranged from 0·022 to 0·025 V. The corresponding values of n are approximately 0·3 and 0·15, and may be compared with the theoretical value 0·25 (equation (19)).

Summary.

1. The method of dimensional analysis is applied to the diffusion and convection processes which govern the transfer of a solute between an electrode and the bulk of a solution, and the results thus obtained are extended by consideration of experimental and theoretical work on the closely analogous subject of heat transfer.

2. The thickness of the diffusion layer at a vertical electrode in unstirred solution is calculated from experimental heat transfer data, in satisfactory agreement with observed values.

3. It is shown that the thickness of the diffusion layer, δ, at an electrode in a stirred solution is independent of the concentration difference between the interface and the bulk of the solution. In unstirred solutions, some variation of δ with concentration difference is to be expected, and the resulting changes in the relation between current and concentration overpotential are briefly discussed.

Résumé.

(1) L'analyse dimensionnelle est appliquée à la diffusion et à la convection, qui régissent le transport d'une substance dissoute entre une électrode et le corps de la solution; les résultats ainsi obtenus sont étendus par comparaison avec des travaux expérimentaux et théoriques sur un sujet analogue, le transport de chaleur.

(2) L'épaisseur de la couche de diffusion sur une électrode verticale en solution non agitée est calculée à partir de valeurs expérimentales du transport de chaleur et se trouve en bon accord avec les résultats observés.

(3) On prouve que l'épaisseur de la couche de diffusion, au voisinage de l'électrode dans une solution agitée, est indépendante de la différence de concentration entre l'interface électrode-solution et le corps de la solution. Dans des solutions non agitées, on doit s'attendre à une certaine variation en fonction de la différence de concentration; les changements qui en résultent dans la relation entre le courant et le survoltage par concentration sont brièvement discutés.

Zusammenfassung.

(1) Die den Übergang von gelöster Substanz zwischen einer Elektrode und der Hauptmenge der Lösung kontrollierenden Diffusions- und Konvektionsprozesse werden mit Hilfe der Dimensionsmethode analysiert. Die Erwägung von experimentellen und theoretischen Arbeiten auf dem eng verwandten Gebiet der Wärmeübertragung ermöglicht eine Erweiterung der so erhaltenen Ergebnisse.

(2) Die aus den Resultaten von Wärmeübertragungsmessungen berechnete Dicke der Diffusionsschicht an einer vertikalen Elektrode in einer ungerührten Lösung stimmt gut mit den beobachteten Werten überein.

(3) Es wird gezeigt, dass die Dicke der Diffusionsschicht an einer Elektrode in einer gerührten Lösung unabhängig vom Konzentrationsunterschied zwischen der Phasengrenzfläche und der Hauptmenge der Lösung ist. Für ungerührte Lösungen ist aber eine solche Abhängigkeit zu erwarten und die dadurch hervorgerufenen Veränderungen in der Relation zwischen Stromstärke und Konzentrationsüberspannung werden kurz besprochen.

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THE THEORY OF CONCENTRATION POLARISATION.

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1. Introduction.

The velocity of electrochemical processes on the surface of an electrode immersed in a solution is governed by two factors: the velocity of approach of matter (ions or molecules) to the electrode and the velocity of the electrode processes proper.

In this paper we shall deal with the first factor. The molecular diffusion of ions in a liquid solution takes place extremely slowly. Therefore in practice the process is accelerated by artificially stirring the solution. It should be observed that if the solution is not purposely stirred then the irregular distribution of the density always gives rise to natural convection. The transport of ions to the surface of the electrode is thus brought about as a rule by convective diffusion.

The magnitude of the current flowing through the electrode depends to an extremely great degree on purely hydrodynamical factors. In a number of papers [1] we have discussed the influence of hydrodynamical factors on the velocity of heterogeneous reactions on interphase boundaries. The electrochemical reactions on the surface of an electrode are a particular case of such processes. The present communication will deal only with such reactions, it being first assumed that the electrode processes take place in the absence of noticeable overvoltage. To simplify the treatment we shall also limit ourselves to the case when the solution contains an excess of a neutral electrolyte.

The problem of the transport of matter in stirred solutions has been the subject of numerous theoretical and experimental investigations. Nernst [2] developed a qualitative theory of this process. He assumed that the main change in the concentration of the solution takes place in a very thin stationary layer contiguous to the electrode surface (Nernst's diffusion layer).

The diffusion current per unit surface area of the electrode is related to the concentration difference and the thickness of Nernst's diffusion layer δ' by the expression:

$$j_{\text{dif.}} = Dn_eF\frac{c_\infty - c_0}{\delta'} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] Levich, *Acta Physicochim.*, 1942, 17, 257; *ibid.*, 1943, 19, 117; *J. Physic. Chem.* (*Russ.*), 1944, 18, 335; *ibid* (in press).

[2] Nernst, *Z. physik. Chem.*, 1904, 47, 52; Nernst and Merriam, *ibid.*, 1905, 53, 235.

where D is the diffusion coefficient of the reacting particle, n_e the change of valency during the electrochemical reaction and c_∞ and c_0 are the concentrations of the solution far from the electrode and at its surface, respectively.

It is postulated in Nernst's theory that the thickness of the diffusion layer is independent of the nature of the electrochemical process on the electrode surface and of the character of the potential distribution. The absolute value of δ' depends on the régime of stirring, and must be found from experiment. In the usual practical cases of stirring, Nernst's diffusion layer has a thickness of the order of $10^{-3} - 10^{-5}$ cm., and depends on the régime of stirring according to the law:

$$\delta' = \frac{const.}{U^n}$$

where U is the velocity of the liquid. The values of n found by different authors[3] vary from $n = 0{\cdot}5$ to $n = 1$.

Although Nernst's theory was very fruitful in its time, it is now somewhat inadequate. In the first place this theory—at any rate, as usually formulated—contains the clearly unpermissible assumption that the liquid is stationary within the diffusion layer, which is contrary to the experimental data on the flow of liquids near solid surfaces.[4] Furthermore, the theory does not allow quantitative predictions to be made and it does not even offer any qualitative indications as to the dependence of δ' on the régime of stirring.

The inadequacy of Nernst's theory induced Eucken to reject the notion of a diffusion layer and attempt to develop a strictly hydrodynamical theory of the transport of matter in a moving solution.[5] Eucken did not, however, give a general theory of the transport of matter in a liquid, while the inaccuracy (see ref. (1)) of his initial equation invalidates his results for practical cases of stirring.

2. Equations of the Transport of Matter in a Moving Liquid.

In all cases of stirring of practical interest the Reynolds numbe $Re = \frac{Ul}{\nu}$ is great compared with unity (and Ul are, resp., the characteristic velocity and dimension, and ν is the kinematic viscosity of the liquid). The flow of the liquid, as is well known, can then be divided into a region of non-viscous flow and the Prandtl boundary layer contiguous to the surface of the solid.

We set ourselves the problem of studying the motion of ions or molecules in a liquid that is being stirred. To solve the problem of the transport of matter in a stirred solution it is necessary: (*a*) to solve the equations of convective diffusion and find the distribution of concentration in the solution, and subsequently (*b*) to find the distribution of the potential.

The equation of convective diffusion to the surface of a solid has the form:

$$U\frac{\partial c}{\partial x} + V\frac{\partial c}{\partial y} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) \quad . \quad . \quad . \quad (2)$$

where c is the concentration and D the diffusion coefficient. The left-hand side expresses convective transport in the moving liquid, the right-hand side, ordinary diffusion. The boundary conditions of the problem are as follow. In the bulk of the solution far from the electrode, the concentration must have a constant value c_∞. At the electrode surface the boundary conditions may vary. In the simplest case of constant potential

[3] Brunner, *Z. physik. Chem.*, 1904, **47**, 56; Nernst and Merriam, *loc. cit.*; Van Name, *ibid.*, 1910, **73**, 9, *Amer. J. Sci.*, 1910, **29**, 237; Wilderman, *Z. physik. Chem.* 1909, **66**, 445; King and Schack, *J. Amer. Chem. Soc.*, 1935, **57**, 1212.

[4] Fadge, *Proc. Roy. Soc. A*, 1932.

[5] Eucken, *Z. Elektrochem.*, 1932, **38**, 341.

the concentration at the electrode surface should have a constant value $c = c_0$. In particular for the régime of the limiting current, $c = 0$ on the electrode surface.

If equation (2) is compared with the equations of motion of a viscous liquid they are seen to be similar, the unknown concentration taking the place of the unknown velocity components in the equations of motion, and the diffusion coefficient that of the viscosity. Hence equation (2) can be solved in the same way as the Navier-Stokes equations in hydrodynamics.

The ratio of the two terms in (2) is in order of magnitude equal to

$$Pe = \frac{U\left|\frac{\partial c}{\partial x}\right|}{D\left|\frac{\partial^2 c}{\partial x^2}\right|} = \frac{Ul}{D}.$$

This dimensionless number is called the Pekle number. It corresponds to the Reynolds number for the flow of a liquid, and the régime of transport of matter is determined by the value of the Pekle number. If this number is great compared with unity, molecular diffusion can be neglected in comparison with the convective transport of matter; if it is small, on the contrary, molecular diffusion predominates.

The ratio of the Pekle and Reynolds numbers is a dimensionless number called the Prandtl number:

$$\frac{Pe}{Re} = \frac{\nu}{D} = Pr.$$

In liquids the Prandtl number is always large compared with unity; for water it is usually of the order of 10^3. In gases, on the contrary, the Prandtl number is of the order of unity.

Due to the smallness of the diffusion coefficient, the Pekle number is large for the lowest values of the velocity, even when the corresponding Reynolds number is still small compared with unity. Molecular diffusion in liquids can therefore almost always be neglected in comparison with the convective transport of matter. When the Pekle number is large convective diffusion can be treated in a manner analogous to that applied in hydrodynamics to the flow past a body at large Reynolds numbers. Thus if the Pekle number is large compared with unity, then the term due to molecular diffusion in (2) can be dropped and the solution of the equation will be $c = \text{const.} = c_\infty$.

The concentration of matter will thus be constant throughout the volume of the liquid. However, this solution of the equation cannot be valid on the electrode surface where the condition $c = c_0$, or $c = 0$, must be satisfied. There should therefore be a thin layer of liquid near the surface of the electrode in which the concentration varies rapidly. In this layer the derivatives of the concentration with respect to the co-ordinates are very large and as a result the term in the right-hand side of (2) expressing molecular diffusion becomes comparable to the term in the left-hand side, despite the smallness of the diffusion coefficient.

Thus, at large Pekle numbers, as at large Reynolds numbers, the entire liquid can be divided into two parts; a region of constant concentration far from the surface of the reaction and a region of rapid variation of the concentration in the immediate vicinity of this surface. The latter extremely narrow zone is analogous to the Prandtl boundary-layer. In the Prandtl layer the viscosity of the liquid must be taken into account, whereas in the main volume of the flow it does not come into play. Similarly, in the liquid layer contiguous to the surface of the electrode molecular diffusion must be considered. This layer will therefore be called the diffusion boundary-layer.

The concept of the diffusion boundary-layer is evidently a generalisation of Nernst's layer. However, the two concepts are fundamentally different

in that the velocity of flow of the liquid in the diffusion boundary-layer is not necessarily equal to zero. On the contrary, the diffusion and convection currents of matter are of the same order of magnitude. The diffusion boundary-layer is an analogue of the thermal boundary-layer in the theory of the transport of heat in liquids, but there is an important quantitative difference between the two: the diffusion boundary-layer is several times thinner than the thermal layer and hence its properties (e.g. the spatial distribution of matter) differ from the analogous properties of the thermal layer. We shall return further to the problem of the limits of applicability of the concept of the diffusion boundary-layer.

On this basis it was possible to develop a qualitative theory of the boundary-layer for an electrode of arbitrary form, using considerations of dimensions and to calculate the diffusion currents and the distribution of potential for a number of geometrically simple cases of flow. Only a short summary of the main results arrived at will be set forth here.

3. Diffusion Currents.

We have found the exact solution of the equations of convective diffusion of ions to an electrode having the form of a large disc revolving about an axis passing through its centre. The c.d. on the electrode is given by an interpolation formula, which coincides with that of Nernst's theory (I), if for the thickness of the diffusion layer we put:

$$\delta' = 1{\cdot}62 \left(\frac{D}{\nu}\right)^{\frac{1}{3}} \left(\frac{\nu}{\omega}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (3)$$

where ω is the angular velocity of the electrode.

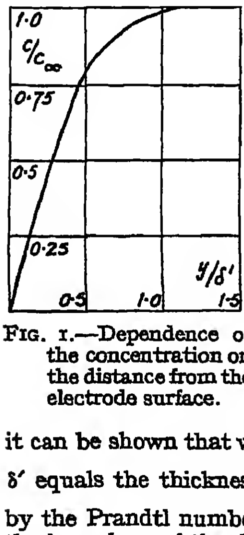

FIG. 1.—Dependence of the concentration on the distance from the electrode surface.

In Fig. 1 is represented the dependence of the concentration of the solution on the distance to the disc (in units of δ'). We see that the main change in the concentration takes place at a distance of unit length so that in this sense δ' really represents the thickness of the diffusion boundary-layer. Comparing δ' and δ, the thickness of the hydrodynamical boundary-layer in which the revolving disc exercises the main drag on the liquid, it can be shown that with an accuracy up to a factor of the order of unity, δ' equals the thickness of the layer dragged along divided by $\left(\frac{D}{\nu}\right)^{\frac{1}{3}}$, i.e. by the Prandtl number Pr to the power $\frac{1}{3}$. The velocity of the liquid at the boundary of the diffusion layer is equal approximately to 10 % of the total velocity of flow and falls off gradually to zero at the solid surface.

The second case to be analysed in detail was that of an electrode in the form of a plate set in a laminar flow of liquid. For the limiting current régime when the concentration of the reacting ion at the electrode surface is zero, the density of the limiting current on the electrode is:

$$j_{\text{lim.}} = 0{,}\ 33\ n_i F D c_{\infty} \left(\frac{D}{\nu}\right)^{-\frac{1}{3}} b \left(\frac{U}{\nu x}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad (7)$$

where U is the velocity of the liquid, b, the cross-section of the plate, x, the co-ordinate along the plate counting from the edge. The thickness of the diffusion layer is:

$$\delta' = 3 \left(\frac{D}{\nu}\right)^{\frac{1}{3}} \left(\frac{\nu x}{U}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the case of a plate the thickness of the diffusion boundary-layer increases as the square root of the distance x from the edge of the plate

and as the inverse square root of the velocity of the liquid. The diffusion boundary-layer is in this case too geometrically similar to the Prandtl boundary-layer, only thinner by a factor of $\left(\frac{D}{\nu}\right)^{\frac{1}{3}}$.

In addition to forced convection we have also considered the case of natural convection to a vertical plate. We furthermore calculated the diffusion current to the surface of an electrode in the form of a plate for the case of turbulent flow in the hydrodynamical boundary layer. The following expression was found for the total diffusion current in a plate of area S at $Pe \gg 1$:

$$J_{turb.} \simeq C_f^{\frac{1}{2}} n_e F c_\infty (Pr)^{-\frac{2}{3}} US \quad . \quad . \quad . \quad . \quad (6)$$

The coefficient of resistance C_f depends on the velocity of flow past the plate, so that $J_{turb.}$ is a complicated function of the velocity. C_f is first proportional to $Re^{-\frac{1}{5}}$ and then varies with Re logarithmically. Thus $J_{turb.} \sim Pr^{-\frac{2}{3}} U^{0.8}$ and at very great Re, $J_{turb.}$ is almost proportional to $U\ Pr^{-\frac{2}{3}}$.

The case of turbulent flow is important above all because, in order of magnitude, the results obtained can be applied to electrodes of non-streamlined form (sphere, cylindrical wire), and also to electrodes having a rough surface or angles, and to the case when the interior of a tube serves as electrode. In such conditions turbulent motion sets in comparatively easily in the boundary-layer and is the most frequent case encountered. It follows from the preceding results that although the properties of the boundary-layer depend on the régime of the motion and on the properties of the diffusing substance, nevertheless the limiting diffusion current can always be represented in a standard form (I).

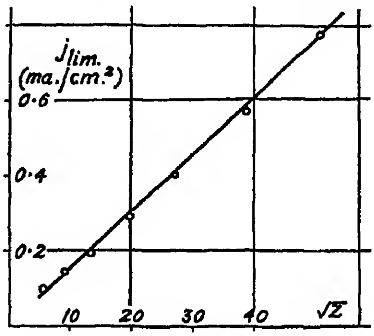

FIG. 2.—Relation between density of limiting current on a revolving disc and number of rotations per min.

Full curve—calculated from eqn. (3) and (1); circles—experimental values (according to Kabanov and Siver).

The author and Meiman recently considered the more general case when the velocity of the electrochemical reaction on the electrode surface is comparable with the velocity of transport of matter to the surface, and also the case when the c.d. on the electrode surface is artificially kept constant (e.g. by introducing a large resistance, which is the same for all the paths of the current).[6] It appeared that for a given régime of stirring and given properties of the ions the thickness of the diffusion boundary layer depends on the velocity of the electrochemical process or on the distribution of potential on the electrode. This circumstance brings out especially clearly the conventional nature of the notion of the diffusion layer which merely represents a convenient and illustrative form of describing the phenomenon and shows that the thickness of this layer is no real physical constant.

The agreement of the theory developed by the author with experiment was checked in the laboratory of Prof. A. Frumkin by Kabanov and Siver for the case of a limiting current on a disc. The electrochemical reaction was the reduction of dissolved oxygen to H_2O_2 on an amalgamated copper electrode. Fig. 2 shows the theoretical curve obtained with the help of

[6] Levich and Meiman, *Acta Physicochim.* (in press).

eqn. (3) and the experimental points. We see that there is complete agreement between theory and experiment.

In the paper cited under ref. (1), the theory was compared with published experimental data on limiting currents. It was shown there that the disagreement between the data of different authors relating to the dependence of n on the velocity, which was mentioned at the beginning of the present paper, is evidently to be attributed to the varying degree of turbulence of the liquid in the different experiments. The dependence of the limiting current on the diffusion coefficient of the ions ($J_{\text{lim.}} \sim D^{\frac{5}{8}}$) and the viscosity of the liquid $\left(J_{\text{lim.}} \sim \frac{D}{\nu}\left(\frac{\nu}{D}\right)^{\frac{3}{8}} \sim \frac{1}{\nu^{\frac{5}{8}}}\right)$ is found to agree with experiment. It is at present impossible to make a quantitative comparison of the formula for the current in the case of turbulent flow in the boundary-layer with the existing experimental data in view of their incompleteness.

In addition to the above calculation of diffusion currents to the surface of a solid electrode we calculated the diffusion to a liquid-liquid interface for a number of cases too.

Diffusion to a liquid electrode presents electrochemical interest in connection with the existence of a tangential motion of the surface of dropping mercury described by Krjukova.[7] This tangential motion stirs up the liquid and gives rise to a current on the dropping electrode which under suitable conditions can be comparable to, or even exceed, the current on a radially growing drop, as calculated by the Ilkovič-Rideal-MacGillavry equation. Hence when tangential motion of the drop is possible the current on the drop increases. This phenomenon has been given the name of a polarographic maximum of the second kind.

Convective diffusion to a liquid interface differs fundamentally from the discussed case of diffusion to a solid surface. This difference results from the change in the hydrodynamical conditions: at a liquid interface the tangential component of the velocity remains continuous and does not vanish as it does at a solid wall. Due to this, the conditions of stirring are much more favourable, and the current is greater than at a solid surface.

A calculation of the current to the surface of the drop yields the following expression for the total current J on the drop:[8]

$$J = 8\sqrt{\frac{\pi}{2}}\left(\frac{DV}{a}\right)^{\frac{1}{2}}(c_{\infty} - c_0)a^2$$

where V is the velocity of the liquid at the surface of the drop and a the radius of the drop. This theory rests on the assumption that the interface is completely mobile, which is not so in the presence of a double electrical layer or of a layer of adsorbed molecules. In this case a number of new phenomena appear which, however, cannot be treated here (effect of a double-layer on the mobility of a liquid-liquid interface),[9] influence of surface-active substances.[10]

The above investigations were undertaken at the suggestion of Prof. A. Frumkin. In the course of the work the author had valuable discussions with Prof. A. Frumkin and Prof. L. Landau, to whom he expresses his sincere gratitude.

Résumé.

On considère la vitesse à laquelle des corps (ions ou molécules) s'approchent d'une électrode, la réaction électrochimique à la surface de l'électrode étant regardée comme un cas particulier de l'influence de

[7] Krjukova, *J. Physic. Chem.* (*Russ.*), 1946, **20**, 1179; *Acta Physicochim.* (in press).
[8] Levich, *Acta Physicochim.* (in press).
[9] Frumkin and Levich, *ibid.*, 1945, **20**, 769; 1946, **21**, 193.
[10] Frumkin and Levich, *ibid.* (in press).

facteurs hydrodynamiques sur la vitesse des réactions hétérogènes aux interfaces. Le traitement suppose qu'il n'y a pas de survoltage notable et que la solution contient un excès d'un électrolyte neutre. On donne la solution des équations qui se rapportent aux deux convections, naturelle et forcée, vers différents types d'électrodes et on compare la théorie avec les données expérimentales connues.

Zusammenfassung.

Unter der Annahme, dass die elektrochemische Reaktion an der Elektrodenoberfläche als ein besonderer Fall des Einflusses von hydrodynamischen Faktoren auf die Geschwindigkeit von heterogenen Reaktionen an Phasengrenzflächen betrachtet werden kann, wurde die Geschwindigkeit, mit der sich Materie (Ionen oder Moleküle) der Elektrode nähern kann, theoretisch untersucht. Es wird dabei weiters angenommen, dass keine Überspannung vorhanden ist und dass die Lösung überschüssigen Neutralelektrolyt enthält. Die Gleichungen werden für natürliche und Zwangskonvektion zu verschiedenen Elektroden gelöst und die Theorie mit in der Literatur befindlichen experimentellen Daten verglichen.

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GENERAL DISCUSSION

Dr. A. K. Holliday (*Liverpool*) said : In the paper of Grimley and Mott, reference is made to the experimental work of Julien, who found a negative ζ-potential at the surface of capillaries of fused AgBr, in the presence of appreciable concentrations of Ag^+ ions. Julien also found that AgBr, freshly precipitated in the presence of excess $AgNO_3$, has a positive ζ-potential, which decreases with time and becomes negative after a few hours ; thus the precipitated AgBr must undergo ageing before it can acquire the negative potential required by the theory of Grimley and Mott. For colloidal AgBr, determinations of the electrophoretic mobility of the particles which I have made indicate that a well-aged and dialysed AgBr sol acquires immediately an appreciable *positive* charge when $AgNO_3$ is added ; for example, 0·01 M. $AgNO_3$ gives a value of ζ not less than -45 mv. Moreover, AgBr particles, in the presence of a saturated solution of AgBr only, have a ζ-potential of practically zero, as against the value of -40 mv. given by Grimley and Mott. Clearly the assumption that the ζ-potential of AgBr is always negative does not hold for the colloidal state, though it may be true for macroscopic crystals. The *immediate* appearance of a positive charge when $AgNO_3$ is added to an initially neutral AgBr sol seems to preclude any possibility that the charge can arise within the solid phase (e.g. by an increase of the concentration of interstitial Ag^+ ions inside the lattice). The conventional explanation, that Ag^+ ions are adsorbed at the surface of the AgBr, is discounted by Grimley and Mott, and I should like to know if they have any suggestion to make regarding the means by which AgBr particles do acquire a positive charge in the presence of an excess of Ag^+ ions.

Mr. C. A. McDowell (*Liverpool*) said: (1) With regard to the results just quoted by Holliday I should like to point out that Julien [1] found that though the negative charge on capillaries of fused AgBr was not reversed by silver nitrate, reversal was obtained when capillaries coated with colloidal AgBr were used. Similar results were observed by Kruyt. He [2] has shown that while the ζ-potential of crushed barytes (as calculated

[1] Julien, *Thesis* (Utrecht, 1933), see Butler, *Electrocapillarity* (Methuen, 1939), p. 121.

[2] Kruyt and Ruyssen, *Proc. Acad. Wetenschappen Amsterdam*, 1934, 37, 624.

from electroendosmosis experiments) is always negative and is not reversed by $BaCl_2$, the ζ-potential of precipitated $BaSO_4$ is positive in the presence of $BaCl_2$. It seems, therefore, that the ζ-potential of a heteropolar surface depends on the origin of the material. It may be that the theory outlined by Mott and Grimley applies to fairly large and reasonably perfect crystals but not to particles of colloidal dimensions.

(2) There has been considerable [3, 4] discussion amongst colloid chemists as to the correct value of D, the dielectric constant of water, to use in calculations involving Poisson's equation and I should like to know if Professor Mott or Mr. Grimley would care to make any remarks about this.

Prof. N. K. Adam (*Southampton*) said: If the silver halide surface is always negatively charged, even in presence of an excess of silver ions over halide in the solution, we shall have to find another explanation of the action of fluorescent indicators, whose coloured anions are generally supposed to become adsorbed when an excess of silver ions in solution charges the surface positively.

Dr. J. A. V. Butler (*London*) said: There is another aspect of concentration polarisation. It is well known that it frequently happens that the substance concerned in the electrode process becomes so reduced in concentration that the potential must change until an alternative process can occur. The time at which this happens, the *transition time*, can be varied enormously by varying the current and is proportional to either $1/i$ or $1/i^2$ according to the circumstances.[5] The calculation of transition times when they are so short that a uniform diffusion layer can hardly be established is a very difficult problem and I should like to ask Dr. Agar if his calculations would be applicable to these circumstances.

Dr. J. N Agar. (*Cambridge*) (*communicated*): Proportionality between the transition time, τ, and $1/i^2$ follows from the well-known treatment of diffusion at an electrode due originally to Sand.[6] This treatment assumes that there is no convection, but the results should be applicable to moving liquids provided $\tau \ll \delta^2/D$, where δ is the thickness of the diffusion layer and D the diffusion coefficient. Under these conditions the concentration changes occurring during the interval τ are restricted to a thin zone of nearly stationary liquid in contact with the electrode, and supply of solute by convection should be negligible. The $1/i^2$ law is, in fact, commonly observed when τ is small.

There does not seem to be any satisfactory explanation of the linear relation between i and $1/\tau$ found at higher values of τ. The problem has been discussed recently by Levich,[7] for the case of a disc rotating at a steady speed. I do not think that dimensional methods would give much help.

Dr. J. Weiss (*Newcastle*) (*communicated*): In a paper which is in the press I have attempted to give an exact treatment of certain cases of mass transfer in heterogenous systems under conditions of (i) laminar flow, (ii) turbulent flow. Although a number of simplifying assumptions had to be introduced to make the mathematical treatment possible the results obtained show a close resemblance to certain empirical and dimensional equations.

Dr. W. F. Berg (*Wealdstone*) (*communicated*): This note is to draw attention to an experimental method for studying concentration distributions, due to Mr. T. R. Scott, then of I.C.I. Alkali Div., Ltd., which allows a close study of two-dimensional diffusion problems. Such studies seem to be called for in electrode chemistry, since there is much speculation and little detailed knowledge on the concentration distribution of

[3] Rideal, *Surface Chemistry* (Cambridge, 1926).
[4] Lewis, *Trans. Faraday Soc.*, 1932, **28**, 597.
[5] Butler and Armstrong, *ibid.*, 1934, **30**, 1173; 1938, **34**, 806; *Proc. Roy. Soc. A*, 1933, **139**, 406.
[6] Sand, *Phil. Mag.*, 1900, **1**, 45.
[7] Levich, *Acta physicochim.*, 1944, **19**, 133.

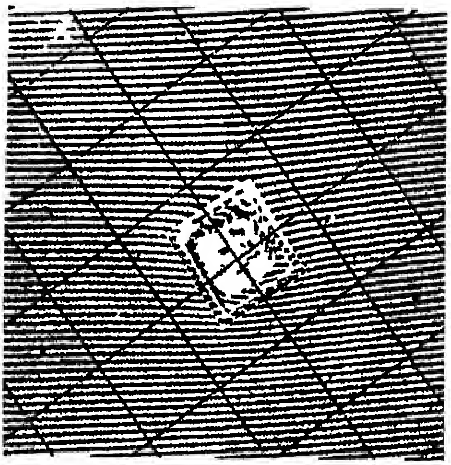

FIG. 1

[To face page 15

ions. An example of the method is shown in Fig. 1.[8] The growing crystal with its surrounding supersaturated solution is held between two heavily surface-silvered optical flats. The system is placed on a microscope stage and illuminated with "parallel" light from a very small source of monochromatic light. The resulting fringes would be straight if the concentration of the solution were constant; the deflection of the fringes allows the concentration distribution to be worked out. The method would seem to be directly applicable to electrode problems, provided that the silver layers on the flats can be insulated from the electrolyte. This should be possible, for example, by evaporating a thin silica layer on top of the silver surface.

Dr. A. F. H. Ward (*Manchester*) (*communicated*): In connection with the papers of J. N. Agar and J. E. B. Randles which involve a consideration of diffusion to an electrode, it may be useful to draw attention to a recent rigorous treatment of this aspect of diffusion.[9] If the solute diffuses, from a constant concentration in bulk, to an interface such as an electrode, the differential equation of diffusion is easily soluble for the simple case when the concentration equals zero at the surface and may also be soluble if the variation of surface concentration with time can be expressed analytically. The new treatment allows the amount of diffusion to be calculated when the concentration at the surface varies with time in any manner whatsoever, provided that values of surface concentration are known at various times. An expression is derived which is amenable to graphical evaluation.

Dr. B. Ershler (*Moscow*) (*communicated*): I should like to make a few remarks concerning the interesting paper of Randles.

Formulæ (16), (17), (18) derived by Randles are identical with formula (2) in my paper [10] and the derivation are identical too. The value R_1 in (18) is equal to r in (2). By comparing Randles' formulæ with (2) one should bear in mind that (16), (17), (18) give the resistance of the electrode without the double-layer and (2) the conductance of the electrode with the double-layer. Therefore by comparing (17) and (2) it is necessary to substitute $\overline{C}$ in (2) by $\overline{C}-C_1$ from formula (1) of my paper, and to calculate the resistance of the scheme consisting of the capacitance $\overline{\overline{C}} - C_1$, and the conductance $\overline{\overline{\Pi}}$ connected in parallel.

It should be mentioned that a theory of the behaviour of an electrode under applied alternating voltage in which the resistances due to concentration polarisation and to retarded electrode reaction are taken in series, was first developed by Frumkin, Dolin and Ershler [11] for the case of a reversible platinum hydrogen electrode. The formulæ derived in this paper were somewhat more complicated since in this case there are two stages of the electrode reaction itself, the discharge of the H^+ ion and the formation of the H_2 molecule.

It is interesting to note that the influence of the nature of the anions present in the solutions on the kinetics of the cation discharge found by Randles can be explained on the basis of Frumkin's correction of the theory of retarded discharge according to which the rate of the cation discharge should increase with increasing negative ζ-potential values.[12] The latter as is known from electrocapillary data actually increases in the series

$$NO_3^- < Cl^- < Br^- < CNS^- < I^-.$$

For the case of the H^+ ion discharge such an influence of the anion was already demonstrated experimentally.[13]

[8] From *Proc. Roy. Soc. A*, 1938, **164**, 79.
[9] Ward and Tordai, *J. Chem. Physics*, 1946, **14**, 453.
[10] *This vol.*, p. 269.
[11] *Acta Physicochim.*, 1940, **13**, 793.
[12] Frumkin, *Z. Physik. Chem. A*, 1933, **164**, 121.
[13] Jofa, Kabanov, Kuchinski, and Chistyakov, *Acta Physicochim.*, 1939, **10**, 317.

Dr. J. H. Baxendale (*Leeds*) (*communicated*): When introducing his interesting paper on the kinetics of rapid electrode reactions, Mr. Randles said that further work on the temperature dependence of the rate constant k had led to the evaluation of activation energies for the reactions. In the experiments reported in the paper the conditions are such that the rate constants of forward and reverse reactions are equal and presumably this applies also to the experiments at higher temperatures. Thus the activation energy measured is apparently that for both the forward and the reverse reactions. But unless the reactions are thermoneutral these cannot be equal, and it appears that the measured activation energy is not in fact the true activation energy. It does involve the heat of the electrode reaction as can be seen from the following.

As stated in the paper the rate constants measured are those for the electrode at *the equilibrium potential*. Using the kinetic picture of electrode reactions [14] we have that, if the electrode is at some potential E with respect to the solution the rate constant for the forward reaction

$$M^{n+} + ne \underset{k_2}{\overset{k_1}{\rightleftarrows}} M(\mathrm{Hg}) \quad . \quad . \quad . \quad . \quad (1)$$

is given by $k_2 = A_2 \exp. (Q_2 + \alpha E)/RT$ and for the back reaction $k_1 = A_1 \exp. (Q_1 - (1 - \alpha)E)/RT$ where Q_1 and Q_2 are the activation energies for the reactions when the electrode is at the same potential as the solution, and αE is the extent to which an applied potential E affects the activation energy of the forward reaction. Now when $k_1 = k_2$, E is the equilibrium potential of the electrode, so that the measured rate constants are functions of the equilibrium potential. Thus the temperature dependence of k_2 is given by

$$\frac{\mathrm{d} \log k_2}{\mathrm{d}(1/T)} = -\frac{Q_2}{R} - \frac{\alpha}{R}\frac{\mathrm{d}(nFE/T}{\mathrm{d}(1/T)}$$

We have for the temperature dependence of the electrode potential

$$\frac{\mathrm{d}(nFE/T)}{\mathrm{d}(1/T)} = -\Delta H,$$

where $H(= Q_2 - Q_1)$ applies to the forward reaction (1) so that the observed activation energy Q is given by

$$Q = Q_2 - \alpha\Delta H = (1 - \alpha)Q_2 + Q_1$$

and it can easily be seen that the temperature dependence of k_1 leads to the same value. It therefore seems that it is not possible to obtain Q_1 and Q_2 from the observed activation energy without a knowledge of α.

Mr. J. E. B. Randles (*Birmingham*) (*communicated*): Breyer and Gutmann [15] derive an expression for the "Dynamic Resistance" and "Dynamic Capacitance" of an electrode on the implicit assumption that the expression relating current to electrode potential for a steady state of the diffusion layer determines the current changes due to an alternating potential of the electrode. It has been pointed out by Ershler and by myself in papers contributed to this Discussion (with reference to an earlier publication [16] by Breyer and Gutmann) that this assumption is inadmissible for alternating potentials of ordinary frequencies since no steady state of the diffusion layer is attained. This will certainly be the case, as stated by Ershler, at all frequencies down to a few C.P.S. It may be worth while to mention that this criticism is supported by the obvious non-correspondence of Breyer and Gutmann's theoretical results with experiment. For instance in their paper expression (4) for R_D makes it independent of frequency which is not true in practice, C_D should be

[14] Glasstone, Laidler and Eyring, *Theory of Rate Processes.*
[15] *This vol.*, p. 19.
[16] Breyer and Gutmann, *Trans. Faraday Soc.*, 1946, **42**, 645.

proportional to $1/\sqrt{\omega}$ which is not shown by expressions (16) and (17), and the statement (p. 25) that "in an ideal perfectly reversible reaction there appears no dynamic resistance" is untrue and is not even in agreement with their expression (4). Elaboration is unnecessary except to remark that the significance of the agreement between experimental and calculated results (Table I) is lessened by the presence of the arbitrary quantity "d" in the latter.

In reply to the useful point made by Dr. Baxendale, I feel it necessary to raise an objection to his implied definition of the "true activation energy" as that which exists when the electrical potentials of the electrode and solution are the same, since this state of equal potential cannot be satisfactorily determined or thermodynamically defined. At the equilibrium potential used experimentally the activation energies of both forward and reverse electrode reactions are equal, apart from any small difference due to difference in the frequency factors A_1 and A_2. These activation energies are equal to Baxendale's expression $Q = (1 - \alpha)Q_2 + \alpha Q_1$ and since it is impossible at present to known Q_1 and Q_2 precisely we must be content with determining Q.

Dr. J. O'M. Bockris (*London*) (*communicated*): The fundamental equations (1) and (8) of Breyer and Gutmann's paper appear to the present author to be quite inapplicable to the dynamic analysis needed for reactions in A.C. fields. The equations given are valid for steady states only.

Dr. B. Breyer and Dr. F. Gutmann (*Sydney*) (*communicated*): Ershler[17] and Randles[18] raised objections as to the applicability of the reversible electrode equation to processes involving superimposed alternating potentials. Ershler states that the general applicability of the equations derived by the present authors is "questionable, in so far as they have been derived from the assumption that at each value of the potential, arising on A.C. charging, a current flows through the electrode equal in strength to the steady state current at this potential. . . . Only on very violent stirring of the solution and at very low A.C. frequencies can the relations obtained by Breyer and Gutmann be valid." Randles states that "That equation refers to what is, in effect, a steady state of the diffusion layer, and is not applicable to the alternating current process."

In the last analysis, Ershler's and Randles' objections centre on the questions, (1) whether the electrode process itself, involving the supply or uptake of an electron by the electrode, is sufficiently fast to allow the application of the reversible electrode equation and (2) whether the diffusion equilibrium would not be disturbed to such an extent as to demand the introduction of some corrections to that equation. It is obvious that of the two processes the second will be the slower.

Randles' own derivations indicate that the ionic distribution round the electrode *can* follow the changes in instantaneous potential at the low frequencies considered. He assumes that the impressed alternating potential will lead to a *harmonic* variation in the concentrations of the ions facing the electrode, with a frequency equal to that of the A.C. and with a *constant* phase angle relative thereto. Randles' experimental results are in accord with the derivations obtained under these assumptions, which therefore can be accepted as justified.

It seems to the present authors, however, that the question raised is important enough to warrant closer investigation. It has to be proved that an ion under the influence of a potential gradient such as exists near the electrode, due to the alternating component of the field, moves fast enough in order to re-establish diffusion equilibrium within $\frac{1}{4}$ of an alternating cycle.

The mobility of, say, Cd ions is approx. 5×10^{-4} cm./sec. for unity field, i.e. for a gradient of 1 v./cm. Nearly the whole of the applied potential appears across the electric double layer formed by the ions facing

[17] Ershler, *this vol.*, p. 45. [18] Randles, *this vol.*, p. 46.

the electrode. This is especially true in the presence of a supporting electrolyte. The bulk of the solution is substantially equipotential. It is generally assumed that the electrochemical processes take place within a space of a few ionic diameters in thickness. From the author's results, however,[19] it follows that the ionic concentration differs markedly from that in the bulk of the solution within a layer always less than $4 \cdot 5 \times 10^{-6}$ cm. thickness. Assuming this latter value, which is the least favourable for the present deliberation, and an R.M.S. value of the superimposed alternating potential of 45 mv., as used by the authors, gives an average field of about 10^4 v./cm. Under this field, an ion will attain an average velocity of approx. 5 cm./sec. At a frequency of 50 C.P.S. therefore, an ion will be able to cover a distance of approx. $2 \cdot 5 \times 10^{-2}$ cm. This distance is about 20,000 times the thickness of the layer, wherein the electrochemical process makes itself felt.

There is also direct experimental evidence justifying the application of the reversible electrode equation to the A.C. processes under consideration. Matheson and Nichols[20, 21] adopted the cathode-ray tube to polarography. They linearly increased the potential applied to the electrode from zero to $- 2 \cdot 4$ v. within 1/60th of a second at a repetition-rate of 30 per sec. Synchronising the dropping rate of the capillary to the repetition-rate yields current-voltage curves exactly in concordance to those obtained in ordinary polarography, on the screen of the cathode-ray tube. These authors also come to the conclusion that "these particular electrode reactions require not more than a few thousandths of a second to attain a steady state." This is in conformity to the present authors' considerations as outlined above. It should be pointed out, moreover, that the rate of change of potential in Matheson and Nichols' case is 144 v./sec., whereas in the present authors' case $|de/dt| = \omega V \sin \omega t$, i.e. a highest rate of 20 v./sec. The mean rate of change will be only 12·7 v./sec. There can be little doubt, therefore, as to the applicability of the reversible electrode equation to the reactions considered.

Referring to Prof. Frumkin's remark[22] as to the lack of a connection between the anomalous trend on his capacity curves and the maxima observed and calculated by the authors, it is desired to state that they accept his point of view.

Dr. B. Ershler (*Moscow*) (*communicated*): As it was shown by Frumkin[23] the electrocapillary zero point can be determined by measuring the capacity of the electrode in dilute electrolyte solutions, the zero point corresponding to the minimum capacity. The minimum capacity values determined experimentally in the case of a mercury electrode (7·8 μF./cm.^{2} in a 0·001 N. solution) are somewhat larger than the theoretical values calculated from Stern's theory.[24] Thus the minimum value 5·75 μF./cm.^{2} found by Breyer and Gutmann, although it agrees with the theoretical value calculated by Frumkin and Vorsina is almost certainly too low.

Dr. B. Breyer and Dr. F. Gutmann (*Sydney*), (*communicated*): In a communication to this Discussion Randles first reiterates his objection to our treatment of electrode reactions in alternating fields on the assumption that the reaction would be too slow to allow attainment of an equilibrium state at the frequency employed (50 c./sec.). We have shown in a communication to this discussion (which probably had not been printed at the time Randles wrote his comment) from theoretical considerations as well as from experimental evidence that this objection cannot be maintained.

[19] Breyer and Gutmann, *this vol.*, p. 24.
[20] Matheson and Nichols, *Trans. Amer. Electrochem. Soc.*, 1938, 73, 193.
[21] Kolthoff and Lingane, *Polarography* (New York, 1941), p. 236.
[22] Frumkin, *this vol.*, p. 57.
[23] *Trans. Faraday Soc.*, 1940, 36, 124.
[24] Vorsina and Frumkin, *Compt. Rend.*, *U.R.S.S.*, 1939, 24, 915.

In his second comment, Randles states that our theoretical results are not in accord with his experimental evidence, since our theory would make the dynamic resistance R_D independent of frequency, which is not true in practice. We wish to point out that Randles has expressed his results in terms of an equivalent *series* circuit while we have treated our case in terms of a parallel arrangement of the dynamic resistance and the dynamic capacitance. If our parallel circuit is transformed into the series arrangement employed by Randles, then by virtue of the well-known transformation equation :

$$R_S = \frac{R_D}{1 + \omega^2 C_D{}^2 R_D{}^2},$$

(where R_S is the equivalent series resistance and R_D and C_D the dynamic resistance and capacitance, respectively), the resulting equivalent dynamic series resistance R_S becomes a function of frequency.

Randles furthermore criticises our treatment because it yields an expression for the dynamic capacitance C_D which is not proportional to $1/\sqrt{\omega}$, as required by Randles' work. In reply to this we wish to point out that the reactions studied by Randles and those treated by ourselves, while closely related, are by no means identical.

Our theory is based upon the continuous passage of direct current. In Randles' experiments there is no direct current present. Therefore the *average* flux of diffusing substance integrated over a whole cycle will be zero in Randles' case, while having a finite value in the processes which we are considering. For zero direct current our theory is inapplicable by its very derivation from the assumption of a steady current flow, exactly as Randles' theory is inapplicable to our case in view of his basic assumption of the absence of a D.C. component. If, in Randles' eqn. (1), a steady term were superimposed upon the alternating one, his solution of the diffusion equation would no longer apply. In Randles' case the flux of diffusing substance is exclusively determined by the alternating current flow. Its average is zero and the reaction rate is governed by the instantaneous alternating potential. In our case, due to the passage of a direct current, the rate of the reaction will be decisively dependent on the rate of diffusion to the dropping-mercury electrode from the bulk of the solution (Ilkovic equation). In other words, in the presence of D.C. the charge density in the proximity of the electrode is primarily governed by the steady current flow and, therefore, less dependent on frequency than in Randles' case.

As to Randles' criticism of our statement, that "in an ideal perfectly reversible reaction there appears no dynamic resistance," we desire to point out that any energy expended in the resistive part of an impedance obviously represents an irreversible loss in contradistinction to that part of the energy which is electrostatically stored in the ionic field and which gives rise to the dynamic capacitance. Our statement referred to an idealised electrode without resistance, a system which certainly cannot be realised in our physical world. In any real experiment the resistance effects have to be considered, as has been done in our eqn. (4) and in the reactions studied by Randles in his eqn. (16).

Our quantity d, which Randles considers arbitrary, has in the meantime been given what we think a rather firm theoretical foundation as the thickness of the "active space" wherein the electrode process occurs. A theoretical treatment giving a mathematical derivation based upon the Debye equation has now been completed by us with the view to publication at an early date.

II. HYDROGEN OVERVOLTAGE.

A CONSIDERATION OF THE MECHANISMS OF ELECTRODEPOSITION REACTIONS AND OVERVOLTAGE.

By A. L. Ferguson

Received 5th February, 1947

Work on the basic question as to the mechanism of electrode reactions was started in the Electrochemistry Laboratory of the University of Michigan in 1920 and has been continued intermittently to the present time. During this period hundreds of oscillograms have been made, dozens of tables of recorded data and curves of various types prepared. To cover this material in the space of 3000 words means confining the paper mostly to general statements, summary remarks and conclusions.

When one stops to think seriously about the various phenomena which take place at the electrode electrolyte interface as current is drawn from a voltaic cell or forced to pass through an electrolytic cell, one is confronted with several very puzzling questions for which no completely satisfactory answers have been given. Some have to do with the simple matter of establishment of a definite potential difference between electrode and solution. These and many more are involved when current is passed either anodically or cathodically through the electrode-electrolyte interface. In all such cases polarisation appears. One of the most interesting and most studied yet least satisfactorily answered, is just what does the additional potential commonly called overvoltage do. The following are some of the more basic problems still unsolved.

1. When a material capable of forming ions is placed in a solution containing some of its ions, a more or less definite potential is almost immediately established. What are the various forces involved and what are the mechanisms by which they operate?

2. It is possible to remove electrons from a metal by several methods. Work is involved commonly called "work function". When a positive ion is discharged at a cathode, an electron must be removed from the electrode. What is the relation between "work function" and electrode potential and overvoltage?

3. In some manner and at some place the electrons and ions must get together at the cathode, and separate at the anode. Does the electron jump through space at the electrode-electrolyte interface?

4. The discharged metal ion becomes a metal atom. These metal atoms are later found located in their proper places in the crystal structure of the deposit. The ions are brought up to the vicinity of the cathode by the potential field in the solution; the metal atoms are directed to their proper places in the cathode by so-called crystallising forces. Do these crystallising forces act only upon the discharged atoms or may they act upon the ion before discharge, and what are the relative magnitudes of these forces?

5. Many substances adhere more or less firmly to the surface of a metal, the force involved is commonly called, for convenience, "adhesion". What part does the force of "adhesion" play in ion discharge and overvoltage?

6. There is much strong evidence that ions are hydrated. What effect does the energy of hydration have upon electrode potential and overvoltage?

7. There are various solvents in which electrolytes may be dissolved. Electrodes placed in such solutions show fairly definite potentials, and when

current is passed overvoltage phenomena appear. The overvoltage values are different in the different solvents. What are the mechanisms by which the solvent influences electrode potential and overvoltage?

8. The electron levels in different metals appear to be different. When two metals are arranged to form a voltaic cell, what relation does the difference in electron levels have to the potential of the cell?

Such fundamental questions as the above are of primary interest to the theoretical chemist; but they are, also, important to industry, since a knowledge of the why and the how of a phenomenon usually leads to better control and development. This is where basic research and industry get together.

In order to secure information which might assist in explanations of the mechanisms of electrode processes, experiments must be made in which they are involved. It was felt the most likely type of experiment would be a study of the nature of the relations between the growth of potential at an electrode immediately after the circuit is closed, and the decay of potential immediately after the circuit is opened. Such measurements must be made under a variety of very carefully controlled conditions.

At the time experimental work was started in this laboratory a serious controversy existed over the proper method for measuring polarisation and overvoltage. Those who supported the direct method, in which measurements are made while the charging current is passing through the cell, contended that the commutator method, in which the potentials are measured while current is not passing, must always give too low values. Those who supported the commutator method contended the direct method must always give too high values. The low values given by the commutator method were explained as due to the observed fact that the polarisation potential decreased extremely rapidly immediately after the polarising circuit was opened; and thus it would not be possible to measure directly the total potential by the commutator method. The too-high values obtained by the direct method resulted from the inclusion in the measurement of electrode potential, of an *IR* drop between the tip of the reference electrode and the electrode under investigation.

It was our feeling that this matter had to be settled before polarisation measurements could be obtained, that would have any real value for an explanation of the mechanism of polarisation potential.

Many years were devoted to this problem. Several methods of attack were used, various pieces of equipment were designed, built, tested, redesigned, rebuilt, etc., etc. It was generally agreed by both sides of the controversy that the key experiment would involve the discovery of a method which would definitely determine the presence or absence of an *IR* drop in the measurement of electrode potential by the direct method.

It had been indicated in previous investigations by others and was definitely demonstrated in our own early work, that the commutator-potentiometer method had certain inherent sources of error which definitely could not be completely eliminated. It was definitely shown that the values obtained on charge by the commutator method as previously measured, were always, by the very nature of the case, higher than the discharge values. After this was demonstrated, the commutator-potentiometer method was discarded.

It became evident that some sort of an oscillograph combined with the commutator or with an arrangement for making measurements by the direct method should give the answer to the problem. A form of oscillograph had been used for this purpose by several investigators many years before; but had been discarded because the high current required polarised the electrodes being measured and thus defeated the purpose of the experiments. This difficulty was eliminated when vacuum tubes became available for amplification purposes.

H. D. Holler, of the National Bureau of Standards in 1923, was the first

to use this new development in connection with the moving-coil oscillograph for the study of polarisation and "transfer resistance". His oscillograms showed vertical sections both at the start of charge and start of discharge, and thus gave strong evidence for the "transfer resistance" theory and against the direct method for measurement of overvoltage. Newbery, who had so vigorously supported the "transfer resistance" theory by his work with the commutator, changed to the cathode ray oscillograph in 1925. Newbery states that his oscillograms "prove conclusively" the existence of "transfer resistance".

Just at the time we were ready to adopt the oscillograph method, the Westinghouse Electric & Manufacturing Company made available the sensitive and supersensitive galvanometers for their Two-Element Power Osiso. By means of this instrument and the proper amplifier it was possible

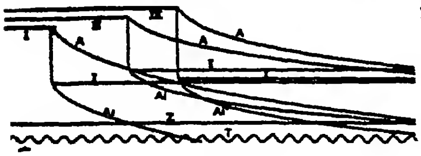

FIG. 1.

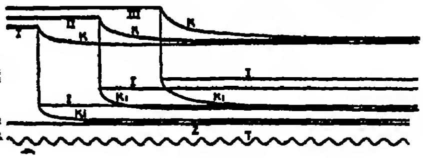

FIG. 2.

FIG. 1.—PALLADIUM ANODE OVERVOLTAGE DECAY CURVES.

Curve.	Potential Measured.	Group I, Sys. I.	Group II, Sys. II.	Group III, Sys. III.
A	Anode — anode standard . .	1·842 v.	1·864 v.	1·873 v.
Ai	Anode — cathode standard . .	1·909 v.	1·991 v.	2·044 v.
I	Anode standard — cathode standard	0·068 v.	0·126 v.	0·171 v.
	Current density (milliamp./cm.^{2}) .	1·70	3·18	4·37

FIG. 2.—GOLD CATHODE OVERVOLTAGE DECAY CURVES.

Curve.	Potential Measured.	Group I, Sys. VI.	Group II, Sys. V.	Group III, Sys. IV.
K	Cathode — cathode standard . .	0·491 v.	0·485 v.	0·484 v.
Ki	Cathode — anode standard . .	1·003 v.	0·831 v.	0·747 v.
I	Cathode standard — anode standard	0·512 v.	0·346 v.	0·263 v.
	Current density (milliamp./cm.^{2}) .	12·26	8·87	6·75

to detect a change in potential of one mv. in 0·0001 sec. A system of automatic electromagnetic controls together with several other pieces of auxiliary equipment made it possible to dispense with the commutator and thus its inherent sources of uncertainty. With this new equipment, hundreds of oscillographs were taken for both anode and cathode charge and discharge curves, for current densities between 20 μa. and 32 ma./sq. cm. All available materials were studied as anodes and cathodes that could be used in 2N. H_2SO_4. Fig. 1 contains exact reproductions of two typical systems of decay curves together with accompanying descriptions and data.

As pointed out above, a potential due to any kind of a resistance such as "transfer resistance", should show a vertical drop when the circuit is opened; and a true active polarisation potential should not show a vertical section. In all of these oscillograms, curve I represents a potential due to the *IR* drop through the solution. It will be observed to drop vertically in all cases. The Ai and Ki oscillograms contain the anode and cathode potentials respectively combined with this same *IR* potential through the solution. The A and K oscillograms contain only the anode and cathode

potentials respectively. It will be observed that the A and K curves contain no vertical sections which means that these potentials do not contain any "transfer resistance". The Ai and Ki oscillograms both contain a vertical section exactly equal to the *IR* drop of the I curves, thus demonstrating that a potential which contains a portion due to *IR*, does drop vertically by an amount equal to the *IR* portion before the gradual decay due to the true electrode potential starts.

In all oscillograms for the various materials, both anode and cathode, and for all c.d.'s used (20 μa. to 32 ma./sq. cm.), there was never a vertical section at the start of charge or of discharge. On the basis of this evidence, it was concluded that over this c.d. range, at least, the direct method for the measurement of polarisation or overvoltage does not contain any part due to an *IR* drop if properly made, and, therefore, is an accurate method for making such measurements. The way was now clear to study intensively the factors that may influence overvoltage and the manner of their action. In all the work that followed, the direct method was used. Several series of investigations were carried out. The first had to do with a phenomenon which had been observed occasionally in the earlier experiments that the charge-current curve, at the start, overshot the final equilibrium value.

These new experiments showed that this was universally true for currents below the decomposition potential and for some distance above. The high values reached became greater as the c.d. increased; but ultimately passed through a maximum and became zero at 31 ma./sq. cm. It was observed, also, that the cathode showed a hump which, however, was much less pronounced and always lagged behind the current.

These results may be explained if it is assumed that the back e.m.f. is due to material actually discharged at the electrode surface by the current even below the so-called decomposition potential. When the circuit is closed, the high initial current is to be expected since the applied voltage is not opposed by a back potential. An excessive current must flow until a back potential is built up by the liberated material which is equal to the applied potential.

A fairly quantitative set of results was obtained in support of this explanation by first applying a potential for about ½ hour or until a stable equilibrium was reached. The circuit was opened for about ½ sec. and then closed. This was done for several c.d.'s between 40 and 176 μa./sq. cm. The peak current values could be determined with considerable accuracy. These values are really *IR* potentials. If it is assumed that the back potential decreases during the interval the circuit is open, due to the removal of some of the active material that caused it, then the applied potential when the circuit is re-closed would be opposed by a smaller back potential than existed when it was opened. It was possible to calculate the instantaneous current to be expected under these conditions when the circuit was re-closed. This, multiplied by the known resistance, should give a value represented by the maximum voltages in the I curve. These maximum voltages varied with current densities from 8·5 to 400 mv. The calculated and measured values agreed within 80 % at the lower range and approximately 100 % at the higher.

This same series of experiments provided other information which supports the explanation that the back potential is due to active material actually set free at the electrode even below the so-called decomposition potential. It was found that the final equilibrium back potential at any given applied potential does not change with length of charge interval. Also, the rate of decay does not depend upon the length of charge interval. The peak values of the I curves after a definite interval an open circuit likewise are independent of the length of the previous charge interval. In other words, these phenomena do not depend upon the quantity of electricity that passed into the electrode. The explanation for this so-called residual current is that it supplies the active material to the electrode

at a rate exactly equal to the rate at which the active material disappears by the various possible methods.

In the work up to this time, numerous observations indicated that the potentials of electrodes on charge and discharge are determined by the amount of active material, such as atomic hydrogen or atomic oxygen, at the electrode-electrolyte interface. If this is true then any factor that altered the rate at which the active material is removed from the interface should influence the electrode potential. The next series of experiments to be described was undertaken to provide information upon this point.

In these experiments the electrodes were polarised by a constant current rather than by a constant potential. Oscillograms were taken of the natural decay of overvoltage of a polarised cathode in both still and stirred solutions. In one set of experiments the solution was saturated with hydrogen and in another, with nitrogen. Oscillograms were obtained for a series of current densities.

The following conclusions based upon these experiments may be stated.

1. The rate of decay in all cases, even where the equilibrium starting potential is below the decomposition potential, is independent of the length of time the current passed before the circuit was opened, which is explained on the assumption that the current merely supplies active material at the same rate it disappears from the electrode-electrolyte interface.

2. The rate of decay in all cases increases with the c.d. used to polarise the cathode. This is to be expected, on the basis of the proposed theory, since the back potential was higher for the higher charging currents, which in turn was due to a higher concentration of active material. This higher concentration would produce a greater rate of diffusion away from the interface.

3. In stirred solutions the rate of decay is greater than in still solutions, which is to be expected since it facilitates the removal of active material from the interface.

4. The stable cathode potential for a given c.d. is most negative in still solutions saturated with hydrogen and is progressively less negative in still solutions saturated with nitrogen, stirred solutions saturated with hydrogen, and stirred solutions saturated with nitrogen. In fact, in the last case, a current of 1 ma. could be passed indefinitely at a cathode potential more positive than the actual reversible value. All of these observations are to be expected from the theory.

5. In still solutions saturated with hydrogen the potential does not decay to the reversible value within several minutes; in solutions stirred by hydrogen, however, the potential decays to the reversible value within 20 to 30 sec. This results from the more rapid removal of active material in the latter case.

6. The rate of decay depends upon other conditions in addition to the potential. These conditions are related primarily to conditions on the solution side of the interface.

7. In solutions saturated with nitrogen, the decay curve passes right through the reversible value with no change in curvature whatsoever. Even in those cases where the stable, polarised potential is more positive than the reversible value, the general form of the decay curve is identical with that when the polarised potential is more negative than the reversible value. These results mean there is nothing particularly characteristic about the reversible value, also that the phenomena in the overvoltage region are in no fundamental respects different from those below the so-called decomposition potential or in the positive potential region. All of these potentials from the lowest to the highest result from the atomic hydrogen liberated by the current and are determined by the activity of this atomic hydrogen and the activity of hydrogen ions in the solution, which latter, however, remains practically constant. The activity in its turn is determined by the relative rate at which the atomic hydrogen is liberated at the electrode and the rate at which it is removed. There are

various ways in which it may be removed such as penetration into the metal, combination to form molecular hydrogen, combination with electrode material, but probably the most important is through diffusion into the solution at the interface and later mechanical removal into the body of the solution.

In the series of experiments just described, no special attention was paid to the charging process. In the next series attention was concentrated on the charge current-potential phenomena at platinised platinum cathodes in 2 N. H_2SO_4 in still and stirred solutions saturated in one case with hydrogen and in the other with nitrogen. All measurements were made with three to seven different electrodes and at different times. The values were reproducible to $\pm$ 0·001 v. In the work involving solutions saturated with hydrogen a constant current was used for charging rather than a constant potential. In the still solutions saturated with nitrogen a constant potential was also used.

The results are summarised in Table I.

TABLE I.—CURRENT-POTENTIAL DATA FOR PLATINISED PLATINUM ELECTRODES IN 2 N. SULPHURIC ACID

Current in Milliamp.	Log₁₀ Current in Amp. × 10⁶.	Stable Polarised Cathode Potential in Volts.			
		Hydrogen Solutions.		Nitrogen Solutions.	
		Still.	Stirred.	Still.	Stirred.
0·0020	0·30	0·000	0·000	+ 0·088	+ 0·092
0·0054	0·73	0·000	0·000	+ 0·038	+ 0·072
0·0096	0·98	— 0·001	0·000	+ 0·022	+ 0·061
0·0196	1·29	— 0·002	0·000	+ 0·015	+ 0·051
0·0468	1·67	— 0·005	0·000	+ 0·006	+ 0·040
0·103	2·01	— 0·007	— 0·001	0·000	+ 0·030
0·132	2·12	— 0·008	—	— 0·001	—
0·224	2·35	— 0·010	— 0·003	— 0·005	+ 0·021
0·452	2·66	— 0·014	— 0·005	— 0·010	+ 0·012
0·895	2·95	— 0·017	— 0·009	— 0·014	+ 0·004
0·911	2·96	—	—	— 0·016	+ 0·003
1·30	3·11	— 0·019	— 0·012	— 0·017	— 0·001
3·85	3·59	— 0·028	— 0·022	— 0·027	— 0·016
7·73	3·89	— 0·035	— 0·030	— 0·034	— 0·026
9·25	3·97	—	—	— 0·037	— 0·030
13·5	4·13	— 0·043	— 0·039	— 0·042	— 0·037
17·5	4·24	—	—	— 0·047	— 0·042

From these results it may be seen that, for the particular system used, about 10 μa. may be passed continuously through the cathode in a still solution saturated with hydrogen without polarising the electrode; in a stirred solution $\frac{1}{10}$ amp. may be passed. In the still solution saturated with nitrogen, a slightly higher current may be used; while the stirred solution required more than 1 ma. continuous current before polarisation started. Since current is passing continuously in these cases, it must be hydrogen ions which are being continuously discharged, in some cases at a potential appreciably positive to the normal hydrogen. This statement is contrary to the assumptions involved in several modern theories of polarisation and overvoltage. As further proof, however, it was observed that at 0·5 ma., bubbles of hydrogen formed at several points on the electrode and escaped into the still solution. This demonstrates that this amount of current liberates hydrogen continuously no matter what the surrounding solution. Reference to the Table, shows that in a stirred solution the electrode is distinctly *positive* to the solution while this same current

(0·5 ma.) is passing. If 0·5 ma. current liberates hydrogen that can be observed in a still solution, there is every reason to believe it does in the stirred solution even though the potential is negative in the former case and positive in the latter.

These results point to the simple explanation that the discharged hydrogen atoms are removed so rapidly that their concentration is not increased sufficiently to build up the back potential to the value equal to that in the still solution. The greater the facility for diffusion from the electrode into the solution, the higher is the current required to maintain a given back potential. Another interesting observation comes to light when the data in columns five and six are plotted against the corresponding log (c.d.) in column two. The former is not a straight line, but contains straight line sections, while the latter approximates much closer to a straight line. The interesting point, however, is that both have straight line sections as the potentials pass from positive to negative values, or in other words, through the theoretical decomposition point. Similar observations were noted in some of the earlier experiments. These results mean that there is no more significance to be attached to the so-called normal hydrogen value than to any other value for a hydrogen potential of a platinised electrode in an ion concentration of unit activity. Whatever is responsible for the potential at the normal hydrogen electrode is no different from that which is responsible for the potential on the positive or " undervoltage " side and on the negative or overvoltage side in the same solution.

There are many theories in the literature to explain overvoltage. Most of them lead to a mathematical relation between the overvoltage and the corresponding current which takes the form $i = a e^{-bV}$. There is an almost frantic attempt to include something that can be called " activation ", also, to include the expression RT/aF, and some sort of a mechanism that will give to a the value 0·5. One gets the impression that more effort is given to accomplish these objectives than to give a comprehensible picture of the mechanism of the process which results in overvoltage. A theory is supposed to explain some phenomenon in terms of other things more generally and easily understood. Some of the modern theories of overvoltage contains involve assumptions and mechanisms which are more complex than overvoltage itself.

The author finds it impossible to account for many of his experimental facts on the basis of any of the modern theories. Most of these facts can be explained, however, by, and support the theory that, the potential of a hydrogen electrode is at all times and under all conditions, whether the value is more positive or more negative than that of the equilibrium value in the same solution, determined by the activity of hydrogen ions and hydrogen atoms at the electrode-solution interface. In other words, the potential is determined by the reaction $H \rightleftharpoons H^+ + e$ which is in stable equilibrium at all times. At potentials more positive than the so-called reversible value, the activity of the hydrogen atoms depends upon the amount of electrode surface covered, and this is determined by the rate of discharge of hydrogen ions and the rate at which the hydrogen atoms thus formed are removed from the interface by all the methods for doing this. One of the most important of these is by diffusion of atomic or molecular hydrogen into the body of the solution or the electrode. At potentials more negative than the reversible value, the potential is still due to the activity of atomic hydrogen at the interface, but much higher currents are needed to maintain these higher activities due to the rapid escape of atomic hydrogen as molecular hydrogen and by the other means.

Résumé.

Les problèmes fondamentaux, concernant l'interface électrode-électrolyte, et encore non résolus, sont brièvement résumés. Les méthodes pour mesurer la polarisation et le survoltage—méthodes du potentiomètre

à commutateur et de l'oscillographe—sont critiquées ; l'auteur donne quelques résultats représentatifs, obtenus avec cette dernière méthode et présente les principales conclusions qu'on en peut tirer. Aucune des théories modernes n'est capable d'expliquer tous ces faits.

Zusammenfassung.

Die fundamentalen noch unaufgeklärten Probleme, die mit der Phasengrenzfläche Elektrode-Elektrolyt verbunden sind, werden zusammengefasst. Die Kommutator-Potentiometermethode und die Oszillographmethode zur Bestimmung von Überspannung und Polarisation werden kritisch besprochen. Typische Resultate, die mit der letzteren Methode erhalten wurden, werden angeführt und die wichtigsten daraus gezogenen Folgerungen dargestellt. Viele der Tatsachen können nicht mit Hilfe der modernen Theorien erklärt werden.

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HYDROGEN OVERVOLTAGE.

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Received 25th March, 1947.

The history of electrochemical kinetics is closely bound with the study of the mechanism of hydrogen overvoltage. This is due both to the great practical importance of the reaction of hydrogen evolution and to the belief in its probable simplicity. The latter, to be true, on the whole has not been confirmed by experiment and to the present day we have no complete picture of the successive stages of this reaction. However, many of its characteristics can be regarded as firmly established. In the present paper we wish mainly to communicate some new results pertaining to this field, in addition to those published in several papers in recent years.[1, 2, 3]

(*a*) Proof that the Rate-determining Stage of the Reaction of Hydrogen Evolution on Cathodes with a High Overvoltage—in particular on Mercury—is the Discharge of the Hydrogen Ion on the Metal Surface unoccupied by Adsorbed Hydrogen.

In this respect considerable interest attaches to a determination of the amount of electrochemically-active substance on the electrode surface from the variation of the potential with time after the current has been interrupted. Hickling and Salt [4] determined potential decay curves and came to conclusions incompatible with the above point of view. The method of extrapolation used by these investigators has been criticised by the present author.[1] In the Karpov Institute of Physical Chemistry, Fedotov recently developed an oscillographic method of registering the potential decay curve on a mercury electrode starting from 5×10^{-6} sec.

[1] Frumkin, *Acta Physicochim.*, 1943, 18, 23.
[2] Jofa and Frumkin, *ibid.*, 1943, 18, 183.
[3] Frumkin and Aladjalova, *ibid.*, 1944, 19, 1.
[4] Hickling and Salt, *Trans. Faraday Soc.*, 1941, 37, 450 ; *ibid.*, 1942, 38, 474.

after breaking the circuit. The electrode capacity can be calculated from such measurements without any additional assumptions only if the overvoltage η varies with the time according to a linear law. For this to be so, it is necessary that the variation of the potential be small compared with RT/F, since in this case the rate of the electrochemical reaction on the electrode after the current has been cut off remains practically constant independently of its mechanism. If these conditions are satisfied then the capacity of the polarised electrode can be calculated by the formula :

$$C = \frac{i_0 t}{\Delta\eta} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where i_0 is the c.d. at the moment of breaking the current, t the time and $\Delta\eta$ the change in the overvoltage. If $\Delta\eta$ is not small compared with RT/F then some assumptions must be made in order to determine the capacity. If there is only one slow stage in the cathode process, then, independently of its nature, the state of the cathode and the rate of the cathode process will be single-valued functions of the potential and hence the c.d. of the spontaneous discharge can be found from the value of the steady current at the same cathode potential. In the case of a mercury cathode the latter is determined by Tafel's formula :

$$i = e^{\frac{\eta - a}{b}}$$

where a and b are constants. Hence for the drop in overvoltage we obtain the expression :

$$\Delta\eta = b \ln \left(1 + \frac{i_0 t}{Cb}\right) \quad . \quad . \quad . \quad . \quad (2)$$

In applying eqn. (2) it is necessary to take into consideration the circumstance that at large c.d.'s the determination of η can be vitiated by the ohmic drop of potential in the solution. A suitable correction can be introduced by measuring the resistance or computing it from the paths of the current ; this correction can be avoided if C is calculated using values of η_{observed} after two different time intervals t' and t'' from the moment of the current interruption.

Fedotov's experiments were carried out with a comparatively large liquid mercury cathode and the c.d. was limited by the condition that the entire surface of the cathode must be uniformly polarised. With i ranging from 5×10^{-6} to 5×10^{-2} he obtained for C values, 18 to 20 $\mu F/\text{cm.}^2$. In other words, even at comparatively large overvoltages the capacity of the double-layer retains its normal value. Thus only ions of the double-layer are detected on the mercury cathode, but not adsorbed hydrogen atoms, the appearance of which would cause a considerable increase in the electrode capacity. This result is in agreement with others previously obtained [1] and is of fundamental importance. Indeed, at small coverage of the surface by adsorbed hydrogen it is possible to draw the unambiguous conclusion that the experimentally observed relation between η and $\ln i$ is incompatible with any other interpretation except that according to which the slow stage of hydrogen evolution on mercury is the discharge stage.

Several authors have advanced the hypothesis that on cathodes with considerable overvoltage atomic hydrogen evaporates into the solution ; this can be detected, e.g., by the reduction of WO_3 suspended in the electrolyte.[5] In this connection the mechanism of the reduction of WO_3 at the surface of a polarised electrode was recently analysed by Bagotzky and Jofa,[6] who found that reduction sets in only when the particles of WO_3 come into immediate contact with the electrode surface and spreads due to the electronic conductance of WO_3 by a mechanism similar to the

[5] Kobosev and Nekrassov, *Z. Elektrochem.*, 1930, **36**, 529.
[6] Bagotzky and Jofa, *Compt. rend., U.R.S.S.*, 1946, **53**, 443.

ordinary action of local elements. Theoretical computations also show that free atomic hydrogen should be expected to appear only at potentials considerably more cathodic than can be realised under normal conditions of electrolysis. It would be incorrect, however, to conclude from the negative results of these experiments that free radicals never appear in the bulk of the solution in electrolytic processes. On the contrary, in other cases, active intermediate products probably can leave the electrode surface and go over into the volume, although this has not yet been proven experimentally.

The most immediate result derived from the theory of slow discharge is the relation between c.d. and the hydrogen ion concentration in the surface layer $(H^+)_s$. This question was again taken over in an investigation recently carried out by Bagotzky in the Electrochemistry Laboratory, Moscow University. If the rate of the over-all process is determined by the rate of the elementary act of discharge of H^+ ions on the metal surface then, regardless of the mechanism of this act, there must be a relation :

$$i = [H^+]_s f(\phi - \psi_1) \quad . \quad . \quad . \quad . \quad (3)$$

where ϕ is the cathode potential and ψ_1 the potential at the point of location of the centre of the hydrogen ion being discharged. Since according to experimental data, the extent of surface covered by hydrogen ions is small, then

$$[H^+]_s = [H^+]e^{-\frac{\psi_1 F}{RT}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to bring eqn. (3) into agreement with the experimental data obtained in 0·1 N. HCl solution, which is in many respects a most convenient object for measurements, it is necessary to put

$$f(\phi - \psi_1) = \exp.\frac{[-(\phi - \psi_1) - a]F}{2RT} \quad . \quad . \quad . \quad (5)$$

where $a = 1{\cdot}460$ (at 20°).

Substituting (4) and (5) into (3) and introducing the overvoltage η instead of the potential ϕ, we obtain

$$\eta = a + \frac{2RT}{F}\ln i + \psi_1 - \frac{RT}{F}\ln [H^+] \quad . \quad . \quad (6)$$

Eqn. (6) was first verified experimentally by Levina and Sarinsky ; [7] they compared the variation of η upon the addition of $LaCl_3$ to HCl solution with the corresponding variation of ψ_1 computed according to Stern's theory. However, as has been shown by measurements of the capacity of a Hg-electrode carried out by Vorsina and Frumkin,[8] in the presence of multivalent cations the double-layer has a more complicated structure than can be accounted for by Stern's theory.* In Bagotzky's investigation the variation of η with the concentration of HCl and the addition of KCl was compared with eqn. (6). ψ_1 was calculated according to Gouy's theory taking into account the finite radius of the ions and putting the capacity of the Helmholtz part of the double-layer equal to 19 $\mu F/cm.^2$. That means that the centres of all the ions are located in the diffuse part of the double-layer which begins at a finite distance from

* The suggestion of Breyer and Gutmann [9] that the anomalous trend of the capacity curves in solutions containing multivalent cations obtained in the experiments of Vorsina and Frumkin is due to the discharge of these ions, is founded on misconception since the observed maxima on the curves lie at potentials at which the possibility of such discharge is excluded ; this was also verified in the experiments by the magnitude of the current passing through the electrode.

[7] Levina and Sarinsky, *Acta Physicochim.*, 1937, **7**, 485.

[8] Vorsina and Frumkin, *ibid.*, 1943, **18**, 242.

[9] Breyer and Gutmann, *Trans. Faraday Soc.*, 1946, **42**, 654.

the electrode surface. This method gives for the variation of ψ_1 with the concentration values which differ little from those obtained by Stern's method of computation. The results of some of Bagotzky's measurements are illustrated in Fig. 1 and 2 for a number of solutions containing HCl and KCl in various concentrations (circles) together with the values of η calculated from eqn. (6).

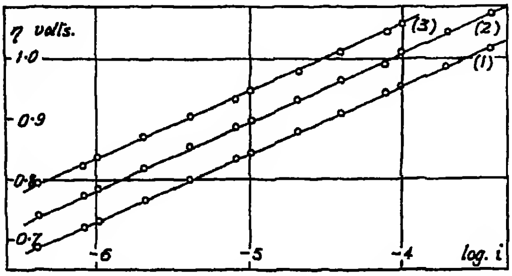

FIG. 1.—Overvoltage against c.d. curves in HCl + KCl, [HCl] + [KCl]=0·1 N.
(1) [HCl] = 0·1 N;
(2) [HCl] = 0·01 N.;
(3) [HCl] = 0·001 N.
Full-line curves—computed by the formula:
$\eta = 1{\cdot}460 + \psi + 0{\cdot}116 \log i - 0{\cdot}058 \log [H^+]$.
o—experimental points.

It thus appears that if agreement between the theory and experiment for 0·1 N. HCl is obtained by suitably choosing a and the dependence $f(\phi - \psi_1)$, then eqn. (6) gives the overvoltage for all other solutions with great accuracy; this proves the correctness of the main assumption of the theory, according to which the reacting particle is the hydrogen ion in the double-layer and the slow stage of the reaction the discharge of this ion. This conclusion does not depend on the theoretical interpretation of the dependence of i on $(\phi - \psi_1)$. The agreement between the theory and experiment is invalidated if the total concentration of the solution exceeds 0·3 N. As appears from Fig. 1, at constant total concentration of the solution and constant i the quantity η varies with $[H^+]$ approximately as $- RT/F \ln [H^+]$. The range of values of $[H^+]$ for which the validity of this conclusion can be proved can be considerably broadened if the potential of the half-wave of the H^+ ion determined with the dropping electrode is used.

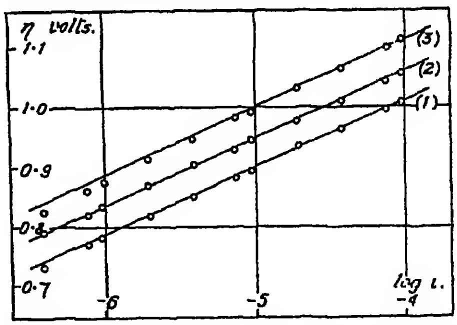

FIG. 2.—Overvoltage against c.d. curves in 0·001 N. HCl in the presence of KCl.
(1) [HCl] + [KCl] = 0·01 N.;
(2) [HCl] + [KCl] = 0·1 N.;
(3) [HCl] + [KCl] = 1·0 N.
Full-line curves—computed by the formula:
$\eta = 1{\cdot}760 + \psi_1 + 0{\cdot}116 \log i - 0{\cdot}058 \log [H^+]$.
o—experimental points.

It is noteworthy that in the case of a mercury electrode the value of the coefficient $b = RT/\alpha F$ in the term containing $\ln i$ in Tafel's equation corrected for the influence of the ψ_1 term gives for α the value 1/2 with an accuracy up to 0·01. It must be conceded that up to date no one has been able to explain why α, in this case at least, is so close to 1/2 and remains constant over such a wide range of potentials. It appears to the author that since the paper by Horiuti and Polanyi,[10] no considerable progress has been made in the interpretation of the coefficient α.

We thought it necessary to dwell in greater length on the verification

[10] Horiuti and Polanyi, *Acta Physicochim.*, 1935, **2**, 505.

of the conclusions following from eqn. (6) since there exists a widespread opinion that the reacting particle is the water molecule and not the hydrogen ion.[11] This concept which is confirmed in the case of hydrogen evolution from alkaline solutions on a Ni-electrode [12] and probably also on a Hg-electrode [13] cannot, however, be applied to acid solutions.[11]

In strong acid solutions at concentrations exceeding N, a considerable lowering of the overvoltage is observed as compared with the value characteristic of dilute solutions. The data on the behaviour of solutions of HCl, HBr, H_2SO_4 and $HClO_4$ on a Hg-electrode are summarised in a paper by Jofa and Frumkin.[3] Jofa [15] investigated concentrated acid solutions on a Pb-electrode and Sindjukov [16] solutions of H_2SO_4 and HCl on a Ni-electrode. The overvoltage in H_2SO_4 and H_3PO_4 on a Hg-electrode was also investigated by Bethune and Kimball.[17] However, their values for the H_2SO_4 solutions lie considerably lower than those found by Jofa; this we believe is due to insufficient care in avoiding contaminations in the solution and on the surface of the mercury electrode. As was shown by Jofa and Frumkin,[3] the lowering of the overvoltage is closely related to the penetration of anions into the double-layer in concentrated solutions. The latter can be detected by measuring the electrocapillary curves and gives rise to considerable negative ψ_1-potentials. The ψ_1-potentials vary linearly with the logarithm of the activity. Ershler attempted to develop a quantitative theory of the structure of the double-layer in concentrated acid solutions which would explain this linear dependence.[18] The nature of the bond between the anions and hydrogen ions at the electrode surface in concentrated solutions cannot, however, be considered established, and it is possible that it is not always purely electrostatic. At any rate, we cannot agree with Bethune and Kimball, who wish to establish a direct relation between the decrease in the overvoltage and the appearance of undissociated acid molecules in the solution. The magnitude of the overvoltage drop is determined not by the bulk properties of the solution, but by the composition of the surface layer. This follows especially clearly from the fact that the overvoltage drop in $HClO_4$ and H_2SO_4, as well as in HCl and HBr at not too high concentrations, decreases strongly with increase in the c.d. and hence, in the negative charge of the surface. Thus in 8 N. $HClO_4$ the decrease in η as compared with 0·1 N. $HClO_4$, when log i varies from -5 to -1, reduces from 0·22 to 0·08 v. At such a total concentration of the acid the concentration of undissociated $HClO_4$ molecules, judging by the Raman effect,[19] is still very small. In concentrated solutions of HCl the electrode potential affects the overvoltage drop considerably less, which perhaps indicates the presence of undissociated HCl molecules in the surface layer. It may also be that the difference in the influence of the electric field of the double layer is due to the different dimensions of the Cl′ and ClO_4' ions.

(b) Comparison of the Rates of the Different Stages of Hydrogen Evolution on Cathodes with Low Overvoltage.

On metals such as Pt which adsorb hydrogen well it is possible to make direct measurements of the rate of H^+ ions. discharge.[20] This was effected

[11] Eyring, Glasstone and Laidler, *J. Chem. Physics*, 1939, **7**, 1053; Kimball, Glasstone and Glassner, *ibid.*, 1941, **9**, 91.

[12] Lukovzev, Levina and Frumkin, *Acta Physicochim.*, 1939, **11**, 21; Legran and Levina, *ibid.*, 1940, **12**, 243; Lukovzev and Levina, *J. Physic. Chem.* (*Russ.*) (in press).

[13] Jofa (unpublished data). [14] Frumkin, *Acta Physicochim.*, 1940, **12**, 481.

[15] Jofa, *J. Physic. Chem.* (*Russ.*), 1945, **19**, 117.

[16] Sindjukov, *Thesis* (Moscow University, 1947).

[17] Bethune and Kimball, *J. Chem. Physics*, 1945, **13**, 53.

[18] Ershler, *J. Physic. Chem.* (*Russ.*), 1946, **20**, 679.

[19] Redlich, *Chem. Rev.*, 1946, **39**, 333.

[20] Dolin and Ershler, *Acta Physicochim.*, 1940, **13**, 747; Rosenthal, Dolin and Ershler, *ibid.*, 1946, **21**, 213.

by means of alternating currents of various frequencies, the current intensity through the platinum electrode being chosen so that the amplitude of oscillation of the electrode potential about a given constant potential did not exceed several millivolts. Under such conditions a platinum electrode with an adsorbed layer of H atoms acts like an admittance composed of a capacitative and a conductance component whose magnitudes vary with the frequency of the current. With increasing frequency the hydrogen layer has no longer time to form and, as a result, the capacitative component of the admittance falls from a value which corresponds to 1200-1400 $\mu F/cm.^2$, i.e. to the "capacity" of the equilibrium atomic layer (at a frequency of 1-50 c.p.s.) to a value corresponding to 30-40 $\mu F/cm.^2$ (at 3000 c.p.s.), i.e., to the capacity of the double-layer, which does not decrease with further increase of the frequency. As for the conductance, it increases with the frequency tending to a limiting value Π which, as has been shown by Dolin and Ershler,[20] is connected with the rate of discharge of H^+ ions by the simple relation:

$$J_0 = \frac{RT}{F}\Pi$$

where J_0 is the c.d. of H^+ ions discharge on a platinum surface at the given potential under equilibrium conditions, i.e., the quantity usually termed exchange current. Experiments carried out by this method made it possible for the first time to measure directly the rate of discharge of H^+ ions under conditions when the formation of molecular H_2 from adsorbed H atoms was excluded. This was accomplished by carrying out the measurements at potentials slightly more anodic than the reversible hydrogen potential, when the equilibrium concentration of molecular H_2 in the liquid becomes sufficiently small. The dependence of the discharge rate on the concentration of H^+ ions found in the case of acid solutions was in satisfactory agreement with the theory of slow discharge of H^+ ions, i.e. the discharge rate at constant hydrogen equilibrium pressure was approximately proportional to the square root of the concentration of H^+ ions.

With increase in the rate of the main electrochemical reaction of discharge, which occurs upon transition to cathodes with low overvoltage, the kinetics of the over-all reaction of H_2 evolution begins to be affected, generally speaking, by the conditions under which the subsequent stages proceed, such as the formation of molecular hydrogen and its removal from the electrode surface. The slowness of these stages is also made manifest by the penetration of hydrogen into the metal.[21] In the case of a palladium electrode it was shown by Frumkin and Aladjalova [3] that the measured overvoltage is additively composed of two components: the first depends on the slowness of the discharge process (of a hydrogen ion or, in the case of alkaline solutions which were primarily used in their investigation, of a water molecule), while the second is determined by the reversible potential of the hydrogen absorbed on the electrode surface. The latter, however, is in equilibrium not with hydrogen at atmospheric pressure, but rather with hydrogen whose concentration is determined by the rate of diffusion in the solution or by the conditions of the $\alpha \rightleftharpoons \beta$ phase transition characteristic of the system Pd—H. The additivity of the equilibrium potential of adsorbed hydrogen and the discharge overvoltage is characteristic of surfaces on which adsorbed hydrogen possesses certain properties, viz., that its fugacity is proportional to $e^{f\theta}$, where f is a constant and θ the extent of surface covered. This relation agrees with the results of direct measurements of the surface covering of a Pt-electrode as a function of the potential at anodic polarisation.[22] Kinetic relations compatible with such thermodynamic properties were deduced by Temkin.[23]

[21] Frumkin, *Acta Physicochim.*, 1937, 7, 475.
[22] Frumkin and Slygin, *ibid.*, 1935, 3, 781; 1936, 5, 819.
[23] Temkin, *J. Physic. Chem.* (*Russ.*), 1941, 15, 296.

According to Dolin and Ershler,[24] in the case of a platinum electrode too, the total overvoltage of H_2 evolution can be divided into two components, one determined by the discharge overvoltage, the other by the rate of diffusion of molecular hydrogen. The first component depends on the concentration approximately in accordance with the conclusions of the theory of slow discharge (the rate of discharge at constant overvoltage in the presence of an excess of a foreign electrolyte is approximately proportional to the square root of $[H^+]$); in alkaline solutions, however, the observed dependence on the concentration does not agree with the theory. This latter circumstance has not as yet been explained.

As Dolin and Ershler have shown, their conclusions are confirmed by comparison of the rate of discharge of H^+ ions measured by the method described above, with the rate of evolution of molecular hydrogen corrected for concentration polarisation in the solution. At first sight a comparison of the rate of discharge with the rate of gas evolution appears difficult since the former is measured at a potential slightly more anodic than the reversible hydrogen potential, inasmuch as only under such conditions the evolution of H_2 can be excluded. The comparison, however, becomes possible due to the previously mentioned properties of adsorbed layers of H on Pt. At medium covering of the Pt surface by adsorbed hydrogen the rate of discharge on the equilibrium electrode ceases to depend on the potential due to mutual compensation of the opposed influences of potential and change in adsorption energy on covering as shown by Temkin.[20, 23] Such a comparison leads to the conclusion that in the case of HCl solutions the rate of discharge of H^+ ions and the total rate of evolution of H_2 are almost the same. In other solutions (H_2SO_4, and especially NaOH) the rate of the first stage is greater than the rate of formation of molecular hydrogen; there is, however, a far-reaching parallelism in the way the two processes are affected by a number of factors (composition and concentration of the solution, poisoning of the electrode). It may be that in this case during the evolution of molecular H_2 only a part of the electrode surface is utilised for discharge due to the limitation of the kinetics by the following stage of recombination. This question demands further investigation.

A detailed investigation was made of the process of hydrogen evolution on nickel in acid and alkaline solutions.[12] The overvoltage was measured as a function of the c.d. at cathodic and anodic polarisation with large and small c.d.'s, and as a function of the composition of the solution; the variation of the potential with the time after breaking the current and the behaviour of the electrode in alternating current were also investigated. The material obtained is too abundant to be discussed in detail here. The best agreement with experiment is obtained on the basis of the following scheme. On the greater part of the Ni-electrode the slowest stage is the discharge of the hydrogen ion or, in alkaline solution, of the water molecule. At the same time there exists an area, comprising but a small part of the surface, for which the rate of the process is limited by the stage of recombination,

$$H + H = H_2.$$

It must also be assumed that surface diffusion between the two kinds of areas is a slow process. With a lowering of the concentration of the acid or alkali the discharge rate at a given overvoltage decreases and, as a result, the reaction on the second type of areas increases in relative importance. In alkaline solutions at concentrations of alkali exceeding 10^{-2} N., all the conclusions from the theory of slow discharge concerning the dependence of the overvoltage on the concentration are well borne out; at lower concentrations of alkali with an excess of foreign electrolyte present, the overvoltage becomes nearly independent of the concentration

[24] Dolin and Ershler, *Acta Physicochim.*, (in press).

when the hydrogen atoms recombination is the slowest stage. It is essential, however, that even on the areas on which the discharge is the slowest stage, the rate of the following stages of removal of hydrogen atoms is not infinitely great compared with the discharge; as a result with an increase in the overvoltage on the Ni-electrode adsorbed hydrogen accumulates in increasing amounts. This can be detected in measurements of the electrode potential decay after the interruption of the polarising current.

In the case of small covering of the electrode surface definite conclusions regarding the reaction mechanism can be drawn from the value of the coefficient b in Tafel's equation. This becomes difficult at large covering since the same value of b can correspond to different mechanisms depending on the way the surface covering affects the free energy of the activated complex. Horiuti and Jkusima [25] have proposed a more general relation which can be used to determine the reaction mechanism. Denote by $\overrightarrow{J}$ and $\overleftarrow{J}$ the true values of the cathodic and anodic currents. Then the measured current i is evidently equal to

$$i = \overrightarrow{J} - \overleftarrow{J}.$$

At $i = 0$, $\overrightarrow{J} = \overleftarrow{J} = J_0$, where J_0 is the "exchange current" under equilibrium conditions.

According to Horiuti and Jkusima

$$\frac{\overrightarrow{J}}{\overleftarrow{J}} = e^{\frac{\eta n F}{RT}} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where n is the number of protons in the activated complex. It follows from eqn. (8) that for small values of η

$$i = \frac{\eta n F}{RT} \cdot J_0$$

and, hence,

$$\left(\frac{\partial \eta}{\partial i}\right)_{i=0} J_0 = \frac{RT}{nF} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Eqn. (9) is closely related to eqn. (7). The value of J_0 can be extrapolated from measurements of i at higher overvoltages at which $\overleftarrow{J} < \overrightarrow{J}$ or it can be directly measured by means of isotope exchange. Unpublished data of Levina show that both methods give close values of J_0. The criterion (9) was used by Lukovzev and Levina to investigate the reaction mechanism in the case of a Ni-electrode in alkaline solutions.[13] It should be observed that an exact determination of $\left(\frac{\partial \eta}{\partial i}\right)_{i=0}$ involves considerable experimental difficulties. The mean of a large number of measurements gives for $\left(\frac{\partial \eta}{\partial i}\right)_{i=0} J_0$ values running from 27 to 15 mv. when the concentration of NaOH varies from 0·3 to 3×10^{-4} N. in the presence of NaCl, which according to eqn. (9) indicates a variation of n from 1 to 2. For a platinum electrode Tolin and Ershler,[24] after correcting the value of η for concentration polarisation, as indicated above, found in this manner $n \sim 1$. It should be observed that Horiuti and Jkusima,[25] using a similar though not quite identical procedure found for Pt in KOH, $n = 2$, whence they concluded that the rate-determining stage of the process is the discharge of the H^+ ion on the H atom with the formation of a H_2 molecule. The cause of the disagreement is as yet not clear.

In general, it can be considered established that for electrodes with

[25] Horiuti and Jkusima, *Proc. Imp. Acad. Tokyo*, 1939, 15, 39.

low overvoltage, in addition to the slowness of the discharge stage, the slowness of the following stages of the process also begins to tell. It is at present still impossible, however, to establish with finality the comparative quantitative values of the velocity of these stages, in particular to what extent the reaction $H + H^+ + \varepsilon \rightarrow H_2$ plays a part simultaneously with the removal of hydrogen according to the mechanism : $H + H \rightarrow H_2$.*

(c) Influence of Oxide Films on the Hydrogen Overvoltage.

The problem of the hydrogen overvoltage is complicated by the circumstance that there are a number of additional factors affecting the rate of hydrogen evolution. One of these is the presence of oxide films on the electrode surface. As was shown by Levina and Platonova [26] and Kabanov and Rosenzweig [27] the presence of oxides on a powdered iron electrode in alkaline solutions considerably increases the hydrogen overvoltage. This can be detected by measuring the potential of an iron electrode, preliminarily subjected to anodic oxidation, on cathodic polarisation. According to Kabanov and Rosenzweig, after the reduction of $Fe(OH)_2$ is completed the hydrogen overvoltage is reduced by 0·25 v. In the presence of an oxide film, too, anomalously high values of the coefficient b in Tafel's equation are observed. The overvoltage in these experiments was computed for a constant value of the c.d. corresponding to the reaction of hydrogen formation. The rate of this reaction was determined from the volume of gas evolved. In this case the authors observed the influence of an oxide film which was unstable at the given polarisation, but which made itself felt in the considerable time needed to remove the film.

As has been shown by Kolotyrkin,[28] the hydrogen overvoltage on a lead electrode changes slowly with time. For example, after passing from high to low values of the polarising c.d., one observes a slow increase in the overvoltage. It is possible that these changes in the overvoltage are also determined by the state of oxidation of the surface and are connected with a slow approach to a stationary state of oxidation, corresponding to the given conditions of polarisation. Due to these variations of the overvoltage the curves of potential decay after the polarising current has been interrupted cross one another for currents of different density.

Under different conditions the presence of oxygen on the surface probably leads to a decrease in the overvoltage.

(d) Kinetics of Hydrogen Evolution upon Spontaneous Dissolution of the Metal.

From the viewpoint of practical electrochemistry special significance attaches to the kinetics of hydrogen evolution upon the spontaneous dissolution of metals. The author,[29] and Hammett and Lorch,[30] were apparently the first to apply the laws of the kinetics of the electrochemical evolution of hydrogen in order to explain phenomena observed in the dissolution of metals. They showed that the proportionality between the rate of decomposition of sodium amalgam in buffer solutions and the square root of the concentration of sodium in the amalgam, discovered by Brönsted and Kane [31] follows directly from Tafel's equation. In this

* The former reaction should make the extent of surface covered by hydrogen independent of the polarisation at large c.d.'s.[21] Contrary to the opinion of Hickling and Salt,[4] however, this does not give rise to a limiting overvoltage value, the existence of which is not confirmed by experiment either.

[26] Levina and Platonova, *J. Physic. Chem. (Russ.)* (in press).
[27] Kabanov and Rosenzweig, *ibid.* (in press).
[28] Kolotyrkin, *ibid.*, 1946, **20**, 667.
[29] Frumkin, *Z. physik. Chem. A*, 1932, **160**, 116.
[30] Hammet and Lorch, *J. Amer. Chem. Soc.*, 1932, **54**, 2128.
[31] Brönsted and Kane, *ibid.*, 1931, **63**, 3624.

deduction it is assumed that the evolution of hydrogen and the ionisation of the metal are two independent electrochemical reactions related only by the common value of the potential of the metal surface. The notion of two independent electrochemical reactions on the same surface was widely developed by Wagner and Traud.[32] In a number of investigations carried out in Moscow it was shown that the laws of hydrogen evolution on metal surfaces are not changed by a simultaneous dissolution of the metal. Tafel's equation with ordinary values of the coefficients remains in force even at potentials more anodic than the stationary potential of spontaneous dissolution. Naturally, in such cases the rate of hydrogen evolution cannot be computed from the current; it was determined from the volume of gas evolved. The solution of lead and nickel in acids [33] and of iron in alkalies [26, 27] was studied from this viewpoint. Apparent deviations from this conclusion may be noted when insufficiently pure metals are dissolved, due to the circumstance that the dissolution changes the composition of the metal surface and the magnitude of the hydrogen overvoltage. If the indicated relation is borne out, the potential and rate of spontaneous dissolution can be found from the hydrogen overvoltage and the anodic polarisation curve.[33, 34] Special interest attaches to the case when the rate of ion exchange between the metal and the solution at equilibrium potentials is not too great compared with the rate of hydrogen evolution. In this case the potential of dissolution of the metal cannot be regarded as an equilibrium potential with respect to a definite concentration of ions in the solution. Such a case is encountered in the dissolution of iron and nickel in acids.

It is usually assumed that the potential of active iron in alkalies saturated with $Fe(OH)_2$ which corresponds to a hydrogen overvoltage of $\eta = 0{\cdot}045$ is the equilibrium potential of the system Fe, $Fe(OH)_2$, OH'. However, measurements of the hydrogen overvoltage and anodic polarisation of Fe in alkaline solution led Levina and Platonova [26] and Kabanov and Rosenzweig [27] to the conclusion that this potential is in reality only the steady-state potential determined by the kinetics of hydrogen evolution and of the anodic dissolution of iron, whereas the true equilibrium potential of this system is several hundredths of a volt more negative.

I shall not dwell here on the comparison of this interpretation of the dissolution of metals with the interpretation based on the theory of local elements which is usually given in the theory of corrosion; this question has been discussed elsewhere.[34, 35]

It follows from the above that when the potential of dissolution of metals cannot be regarded as an equilibrium potential with respect to the ions in the solution it should vary when substances affecting the kinetics of the cathodic or anodic processes are introduced into the solution. Kusnezov [36] investigated the action of a large number of organic compounds (corrosion inhibitors) on the steady state potential of dissolution of iron in acids; his findings are in agreement with the viewpoint hero developed.

Although the discharge of hydrogen ions and the ionisation of the metal in the process of dissolution of a metal in aqueous systems are undoubtedly as a rule statistically independent, in principle cases are possible when both processes occur simultaneously in one elementary act. It would be very interesting to draw the line between two such types of reactions.

[32] Wagner and Traud, *Z. Elektrochem.*, 1938, 44, 391.
[33] Frumkin and Kolotyrkin, *Acta Physichochim.*, 1941, 14, 469; Kolotyrkin and Frumkin, *Compt. rend.*, *U.R.S.S.*, 1941, 33, 445, 450.
[34] Frumkin, *Trans. 2nd Meeting on Metal Corrosion* (Academy of Sciences, 1940), 1.
[35] Levich and Frumkin, *Acta Physicochim.*, 1943, 18, 325.
[36] Kusnezov, *J. Physic. Chem.* (*Russ.*) (in press).

Conclusions.

It can be shown by a number of independent methods that in the case of hydrogen evolution on mercury from acid solutions the slowest stage of the reaction is the discharge of the hydrogen ion which completely determines the kinetics of the overall reaction. In the case of cathodes with low overvoltage the rate of the discharge stage can be determined experimentally too ; however, besides this stage the kinetics is also affected by the subsequent stages, such as the formation of hydrogen molecules, or the diffusion of molecular hydrogen in the solution. The presence of oxide films on the surface of metals has a marked influence on hydrogen overvoltage. The hydrogen overvoltage remains unchanged when the anodic process and dissolution of the metal occur simultaneously thus making it possible from measurements of hydrogen overvoltage and anodic polarisation of the metal to draw conclusions regarding the steady-state potential and the rate of dissolution of the metal.

Résumé.

On montre, par diverses méthodes indépendantes, que l'étape la plus lente dans le dégagement de l'hydrogène, sur le mercure à partir de solutions acides, est la décharge des ions hydrogène et ceci détermine complètement la cinétique de la réaction d'ensemble. Avec des cathodes à faible survoltage, la cinétique est alors affectée par la formation suivante de molécules d'hydrogène ou par la diffusions de l'hydrogène moléculaire dans la solution. On discute comment des films d'oxydes influencent le survoltage d'hydrogène et on montre comment, dans certaines conditions, les mesures de ce survoltage et de la polarisation anodique du métal permettent de tirer des conclusions, en ce qui concerne le potentiel de l'état stationnaire et la vitesse de dissolution du métal.

Zusammenfassung.

Eine Reihe von voneinander unabhängigen Methoden haben ergeben, dass die Entladung der Wasserstoffionen die langsamste Stufe der Wasserstoffabscheidung von Säurelösungen an Quecksilber ist und die Kinetik der Gesamtreaktion völlig bestimmt. Bei Kathoden mit kleiner Überspannung wird die Kinetik auch durch die darauffolgende Wasserstoffmolekülbildung oder Diffusion des molekularen Wasserstoffs in der Lösung beeinflusst. Die Wirkung von Oxydfilmen auf die Wasserstoffüberspannung wird besprochen und es wird gezeigt, auf welche Weise, unter gewissen Umständen, Messungen der Wasserstoffüberspannung und der anodischen Polarisation des Metalls zu Schlussfolgerungen über das Gleichgewichtspotential und die Auflösungsgeschwindigkeit des Metalls führen können.

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SOME ELECTRON TRANSFER PROCESSES IN HETEROGENOUS SYSTEMS. PART I. ELECTRODEPOSITION OF HYDROGEN.

By J. Weiss.

Received 26th March, 1947.

I.

The irreversible formation of hydrogen in electrolysis is governed by Tafel's equation which relates the overpotential (η) on the cathode to the current density (i) and is given by: [1]

$$\eta = a + b \log i$$

where a and b are constants. The constant b is of particular interest as it can assume the same value for a number of different electrodes. In general, the value of b depends on the nature of the electrode surface and one can divide electrodes roughly into two groups. (i) Electrodes of high adsorptive power showing low overvoltage (as, for instance, platinised platinum and palladium) with b values of 0·05 to 0·08 ev. (at room temperature). (ii) Electrodes of relatively low adsorptive power such as Hg, Ni, Ag, Cu exhibiting relatively high overvoltage with b values of about 0·11 ev. (at room temperature). Lead (in acetate solution) and tantalum in sulphuric acid show exceptionally high overvoltage with b-values of about 0·2 ev.

The modern theory of overvoltage which is due mainly to Volmer and Erdey-Gruz [2] and Gurney [3] is based on the assumption that the rate-determining process is the neutralisation of the hydrogen ions on the cathode and not the recombination of the hydrogen atoms as was assumed previously by Tafel, which would give a theoretical b-value of $\frac{1}{2}\, 2{\cdot}3RT/F$ (= 0·029 ev. at 20° c.). The present state of the theory is not entirely satisfactory as a number of arbitrary assumptions are still necessary to explain the b-values obtained under different conditions.

It is of great importance that the hydrogen atoms (formed by the electron transfer) primarily appear in the *adsorbed* state on the surface of the electrode. The gain of the adsorption energy of the H atoms is of decisive importance from the energetic point of view and thus only hydrogen ions (adsorbed) on the cathode surface can be discharged, which follows from considerations analogous to the Franck-Condon principle.

II.

It is known, particularly from Tamm's work,[3] that according to quantum mechanics the surface of a crystal (metal) provides additional allowed energy levels for the electrons. The number of these surface electronic levels is proportional to the number of surface atoms (including those of cracks and crevices). On the other hand even relatively slight chemical changes of the electrode surface can *also* provide additional surface energy levels for the electrons. These chemical changes of the electrode surface apart from impurities and changes due to the solvent are primarily due to the hydrogen formed. The surface electronic levels are thus closely connected with the physical and chemical state of the surface.

[1] cf. Glasstone, *Text-book of Physical Chemistry* (London, 1940).
[2] Volmer and Erdey-Gruz, *Z. physik. Chem.*, *A*, 1930, **150**, 203.
[3] Gurney, *Proc. Roy. Soc. A*, 1932, **134**, 137.

It is at once clear that the electrons coming from the interior of the metal *must* pass through the surface (i.e. *through the surface levels*) before eventually reaching the hydrogen ions adsorbed on the electrode. These surface electronic levels must therefore be of considerable importance for the course of processes of this kind.

The electrolytic formation of molecular hydrogen can then be described by the following reactions (s denotes the unoccupied and s^- the occupied surface electronic states):

$$\text{electron (from interior)} + s \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} s^- + \text{hole} \qquad (1)$$

$$s^- + H_3O^+|_{surf} \underset{k'_2}{\overset{k_2}{\rightleftharpoons}} \underset{\text{(adsorbed state)}}{s \ldots H} + H_2O\,^* \qquad (2)$$

$$2s \ldots H \underset{}{\overset{k_3}{\rightleftharpoons}} H_2 + 2s. \qquad (3)$$

This scheme includes a variety of possible kinetic equations. We shall confine ourselves to the discussion of two important (limiting) cases which will illustrate the importance of the surface electronic levels. The following notations indicate the electronic energies along a line perpendicular to the surface of the electrode with respect to an electron outside the metal (in vacuum).

χ, work function of the electrode metal,
V $(= V_r + \eta)$, total potential difference at the electrode,
(V_r, reversible potential; η, overpotential),
I_H, ionisation energy of hydrogen atom,
W_{H^+}, hydration energy of the proton,
ΔA, adsorption energy of a hydrogen atom on the surface of the electrode (more exactly the difference between the adsorption energy of hydrogen atoms and hydrogen ions),
ξ, (mean) binding energy of the electrons in the surface electronic levels.

Case 1.

This represents the case of electrodes generally of low overvoltage where the discharged hydrogen atoms are strongly adsorbed and which corresponds to the relative low electronic level (h) of depth Δ_1 (on account of the relatively large positive value of $\Delta_1 A$). In this case it is to be expected that the surface electronic levels lie *higher* than the electronic levels in the adsorbed H atom. However, the electrons must first pass through the surface electronic levels after which the hydrogen ions can be neutralised. This corresponds to the reactions (1) and (2) in the *forward* direction. Bearing in mind that for instance the electronic transition (1) is governed by the factor $e^{\frac{(\chi - \epsilon V - \xi_1)}{kT}}$, one obtains for the stationary state from eqn. (1), (2) and (3):

$$\frac{d(s^-)}{dt} = k_1\, e^{-\frac{(\chi - \epsilon V - \xi_1)}{kT}} - k_2(s^-)[H_3O^+]_{surf} = 0 \qquad (4)$$

$$\frac{d(s \ldots H)}{dt} = k_2\,(s^-)[H_3O^+]_{surf} - 2k_3(s \ldots H)^2 = 0 \qquad (5)$$

which yields: (F, electrochemical equivalent; i, current density)

$$-\frac{d(H_2)}{dt} = \frac{i}{F} = k_2(s^-)[H_3O^+]_{surf} = \kappa_1 e^{-\frac{(\chi - \epsilon V - \xi_1)}{kT}} = \bar{\kappa}_1\, e^{\frac{FV}{RT}} \qquad (6)$$

* This can be replaced by $s^- + H_2O \rightleftharpoons s \ldots H + OH^-$ under certain conditions.

taking the logarithm and after rearranging:

$$V = (V_r + \eta) = \frac{2{\cdot}3RT}{F} \log \overline{\kappa_1} F + \frac{2{\cdot}3RT}{F} \log i \quad . \quad . \quad (7)$$

and

$$b = \frac{d\eta}{d \log i} = \frac{2{\cdot}3RT}{F} (= 0{\cdot}058 \text{ ev., } 20^\circ \text{ c.}) \quad . \quad . \quad (7a)$$

Thus in this case $\alpha = 1$.

Case ii.

This represents the case of electrodes of high overvoltage, i.e. where the H atoms are only weakly adsorbed ($\Delta_2 A$ small) and which corresponds to the higher electronic level Δ_2. If the surface levels are *lower* than the electronic levels (h) the reaction is represented by the transitions (1), (1′) and (2) corresponding to the equilibrium (1) and reaction (2).

For the stationary state one obtains as before:

$$\frac{i}{F} = \frac{d(H_2)}{dt} = k_2(s^-)[H_3O^+]_{surf} \quad . \quad . \quad . \quad (8)$$

The concentration of (s^-) can be calculated easily assuming that the equilibrium (1) is practically always established (i.e. k'_1 (holes) > $k_2[H_3O^+]_{surf}$

Thus one obtains:

$$\frac{(s^-)^2}{\quad} = K_1' e^{-\frac{(\chi \quad \epsilon V \quad \xi_2)}{kT}} \quad . \quad . \quad . \quad (9)$$

where K_1' represents the entropy term and N_0 the number of electrons in the lower band. As $N_0 \gg (s^-)$, one obtains from eqn. (9):

$$(s^-) \sim \sqrt{N_0 K_1'}\, e^{\frac{(\chi \quad \epsilon V \quad \xi_2)}{2kT}} \quad . \quad . \quad . \quad (10)$$

Introducing this into eqn. (8) this yields:

$$\frac{i}{F} = k_2 [H_3O^+]_{surf} \sqrt{N_0 K_1'}\, e^{\frac{(\chi \quad \xi_2)}{2kT}} . e^{\frac{FV}{2RT}} \quad . \quad . \quad . \quad (11)$$

Taking the logarithm and after rearrangement:

$$V = (V_r + \eta) = const. + 2\frac{2{\cdot}3RT}{F} \log i \quad . \quad . \quad (11a)$$

and

$$b = \frac{d\eta}{d \log i} = 2\frac{2{\cdot}3RT}{F} (= 0{\cdot}116 \text{ ev. at } 20^\circ \text{ c.}) \quad . \quad . \quad (11b)$$

and $\alpha = 0{\cdot}5$.

It is clear that b-values greater than these can be understood in a similar way. These occur with those metals (Pb, Ta) where the electrode surface is more obviously chemically changed. It is reasonable to suppose that in those cases more than one type of surface electronic levels is present.

When in addition to the surface levels s there are also surface levels s_1 (situated between s and h) one may have additional transitions corresponding to the equations:

$$s^- + s_1 \rightleftharpoons s_1^- + s \quad . \quad . \quad . \quad . \quad (12)$$

followed by:

$$s_1^- + H_3O^+|_{ads} \rightarrow s \ldots H + H_2O \quad . \quad . \quad (12a)$$

[4] (*a*) Topley and Eyring, *Nature*, 1934, **133**, 292; (*b*) Topley and Eyring, *J. Chem. Physics*, 1934, **2**, 217; (*c*) Weiss, *Naturwiss.*, 1935, **23**, 64; (*d*) Butler, *Proc. Roy. Soc. A*, 1936, **157**, 423.

[5] (*a*) Tamm, *Physik. Z. Soviet Union*, 1932, **1**, 722; (*b*) Shockley, *Physic. Rev.*, 1939, **56**, 317; (*c*) Pollard, *ibid.*, 1939, **56**, 324.

[6] cf. Fowler, *Statistical Mechanics*, 2nd ed. (Cambridge, 1936), p. 397.

If it can be assumed that equilibrium (12) is practically established it can easily be shown that this mechanism could lead in the first approximation to a b-value of $\sim 4\left(\frac{2{\cdot}3RT}{F}\right) = 0{\cdot}23$ ev. at 20° c. $(\alpha = 0{\cdot}25)$.

Added in Proof.

The following special case is of considerable importance if the surface is covered with hydrogen atoms. In this case s and s^- in the above equations are replaced by $(s \ldots H)$ and $(s \ldots H^-)$ and the discharge reaction takes the form:

$$s \ldots H^- + H_3O^+|_{surf} \rightleftarrows H_2 + H_2O + s \qquad . \quad . \quad (2')$$

which corresponds to the "electrochemical (recombination) mechanism". This leads to a value of $b = \frac{1}{2}\frac{2{\cdot}3RT}{F}$ $(= 0{\cdot}029$ ev. at 20°) as in the original Tafel theory.

Similarly, if apart from equilibrium (1), equilibrium (2) also can be regarded as practically fully established (which is only to be expected in the case of very low overvoltage) the recombination of the hydrogen atoms becomes the time-determining process.

Résumé.

Le développement de la théorie de la décharge a été poursuivi en tenant compte des niveaux électroniques de l'électrode et en examinant le transfert d'un proton de l'état hydraté aux états adsorbés en surface à la cathode. Des niveaux électroniques de surface peuvent être fournis par des impuretés, par des charges chimiques portées par le solvant ou par des atomes hydrogène adsorbés. Dans ce dernier cas, le mécanisme de décharge est identique à celui d'une recombinaison électrochimique lente. On discute une série de cas limites, qui conduisent à des valeurs-α définies entre 0·25 et 2, tandis qu'un traitement plus poussé des équations pour l'état stationnaire peut mener à toute valeur comprise entre ces deux extrêmes.

Zusammenfassung.

Die Entladungstheorie ist weiter entwickelt worden durch Mitberücksichtigung der Elektronenzustände der Elektrode und durch Untersuchung des Übergangs eines Protons vom hydratierten Zustand zum Zustand der Adsorption an der Kathode. Energiezustände für Elektronen an der Oberfläche können durch Verunreinigungen, durch das Lösungsmittel hervorgerufene chemische Veränderungen oder adsorbierte Wasserstoffatome ergeben werden. Im letzteren Fall ist der Mechanismus der Entladung mit dem der langsamen elektrochemischen Wiedervereinigung identisch. Eine Reihe von Grenzfällen, die zu α-Werten zwischen 0·25 und 2 führen, werden besprochen, während eine ausführlichere Ausarbeitung der Gleichungen für den stationären Zustand zu allen dazwischenliegenden Werten führen kann.

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THE THEORY OF OVERVOLTAGE.

By René Audubert.

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The mechanism of the discharge of ions on a metallic electrode is without doubt very complex, but recent work [1] has provided data which now allow the interpretation in a satisfactory manner of a large number of experimental facts and give to these researches a new orientation which is full of possibilities.

Like chemical reactions, electrochemical processes require an activation energy; but the reaction of which the electrodes are the site during the phenomenon of discharge of ions cannot be treated by the ordinary kinetic laws; the speed of the reaction at the electrode is influenced by the electric field. If one designates by V, the difference of potential between the electrode and the portions of the electrolyte which are adjacent to it, by ϵ the electronic charge and by z the valency of the ion, then the characteristic activation energy w of the process considered must be diminished by a term $\alpha z \epsilon V$ where α is an energy transfer factor less than unity.

Theory of Discharge.

The ions in solution are generally hydrated. In these conditions, the discharge must be accompanied by dehydration of the ion. In the case

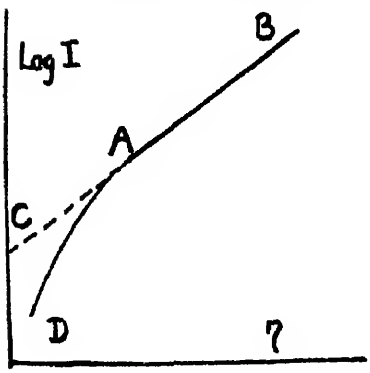


Fig. 1.

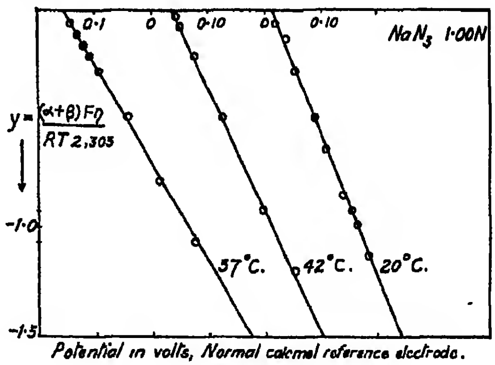


Fig. 2.

of a monovalent cation, for example, the process may perhaps be represented by:

$$M^+_{aq} + e \longrightarrow M.$$

The heat of dehydration of ions is often considerable (e.g. of $H^+ = 250$ kcal.); it may therefore be supposed that the major part of the activation energy is represented by the work of dehydration. Applying Boltzmann's principle, the current density is given to a first approximation by

$$I = k[M^+]_s \, e^{-\frac{w - \alpha FV}{RT}} \quad . \quad . \quad . \quad . \quad (1)$$

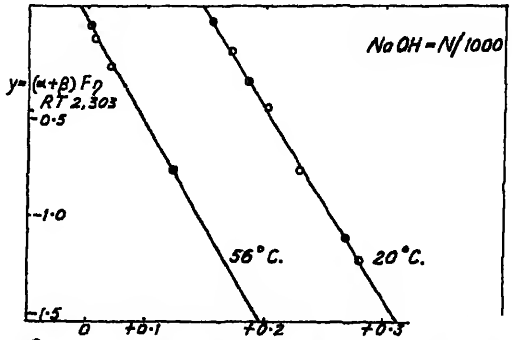
where $(M^+)_s$ denotes the activity of the ion in the layers immediately

[1] Volmer and Erdey-Grúz, *Z. physik. Chem.*, 1930, **150**, 203. Gurney, *Proc. Roy. Soc. A*, 1931, **134**, 137. Audubert, *J. Physique Rad.*, 1942, **3**, 81. Audubert, *J. Chim. Physique*, 1924, **21**, 351. Audubert and Cornnevin, *ibid.*, 1941, **38**, 46. Audubert and Quintin, *ibid.*, 1942, **39**, 92. Audubert and Verdier, *Compt. rend.*, 1941, **213**, 870. Bonnemay, *ibid.*, 1946, **222**, 793; 1946, **223**, 76. Frumkin, *Acta Physicochim.*, 1943, **18**, 23; 1940, **12**, 481.

adjacent to the electrode. But if the inverse processes of ionisation are taken into account, one has

$$I = k[M^+]_s e^{-\frac{w-\alpha FV}{RT}} - k'[M] e^{-\frac{w'+\beta FV}{RT}} \quad . \quad . \quad (2)$$

where (M) is the activity of the atoms, w' the activation energy of the ionisation process and β the corresponding transfer coefficient. Neglecting the second term of this equation, one therefore obtains the empirical Tafel formula ($V = a + b \log I$) which is only verified as is known, in a certain region of overvoltage and best for the least oxidisable elements (Cu, Hg, Ag, Au): the weak ionisation process of these metals plays, however, an important part with oxidisable elements such as Na, K, Mg, Al, Zn, etc.

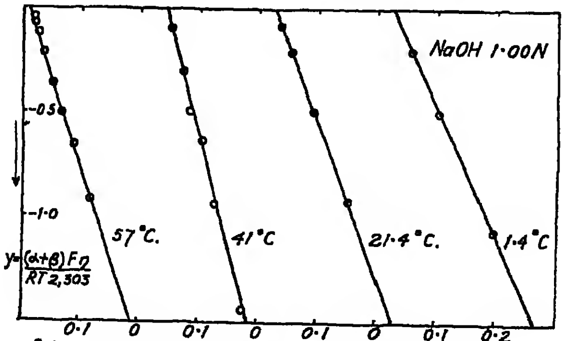


Potential in volts, Normal calomel reference electrode.

FIG. 3.

It is logical to admit that in many cases the speed of discharge is smaller than that of the passage of the atom to a crystalline state (metallic deposits) or to a molecular state (H^+, OH^-, N_3^-, Cl^- etc.); in these conditions the concentration or the activity of the atomic phase varies little as a function of the overvoltage and remains sensibly equal to the value at the thermodynamic equilibrium. Applying therefore the conditions of equilibrium ($I = 0$) to eqn. (2), where V_e designates the potential of the electrode at equilibrium:

$$I = k[M^+]_s e^{-\frac{w}{RT}} e^{\frac{\alpha FV}{RT}} \left[1 - e^{-\frac{(\alpha+\beta)F\eta}{RT}} \right] \quad . \quad . \quad (3)$$



Potential in volts, Normal calomel reference electrode

FIG. 4.

in which the overvoltage η is given by $\eta = V - V_e$. Neglecting the electrokinetic potential, which is usually small, $(M^+)_s$ represents the concentration or the activity in the remote regions of the liquid and V the potential of the electrode.

Verification of the Theory.—Eqn. (3) may be submitted to the control of experiment. Thus, if one plots as abscissæ the values of overvoltage, and as ordinates the corresponding values of log I, a curve is obtained of which the general shape is represented in Fig. 1. The linear portion AB

corresponds to Tafel's equation, the slope of this part allows the determination of the transfer coefficient α; its point of contact with the vertical axis gives the value of $k\,e^{-\frac{w}{RT}}$; finally, the deviation between the produced portion and the curved portion obtained experimentally for low overvoltages gives for each point the value of the term $e^{-\frac{(\alpha+\beta)F\eta}{RT}}$, that is to say, in the last analysis, of β

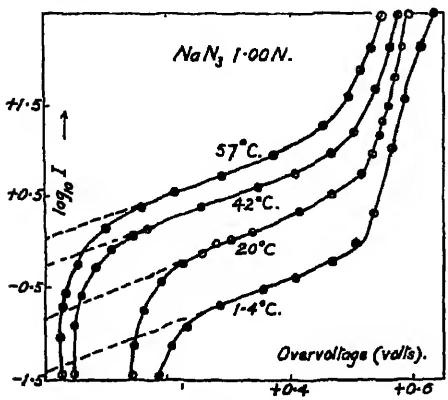


FIG. 5.

The discharge of a number of ions, (H^+, CO^{++}, Cu^{++}, Cu^+, Hg_2^{++}, Hg^{++}, Po^{++++}, OH^-, N_3^-, and the anodic polarisation of Ta, Mg, Al, Si) has thus been studied. These experiments have been made with different salts at several concentrations and several temperatures.

From these researches the following conclusions may be drawn.

1. In the case of discharge of anions, eqn. (3) applies; in all cases the values of α and β are less than unity as required by the theory. Fig. 2, 3 and 4, which relate respectively to the overvoltage of N_3^- and of OH^-, show that the function $y = \frac{(\alpha+\beta)F\eta}{RT}$ varies exactly linearly with the potential of the electrode as required by the theory. Fig. 5, 6 and 7 represent the curves for the overvoltage of the same ions. Two linear portions may be distinguished, to which correspond two values of the transfer coefficient, α.

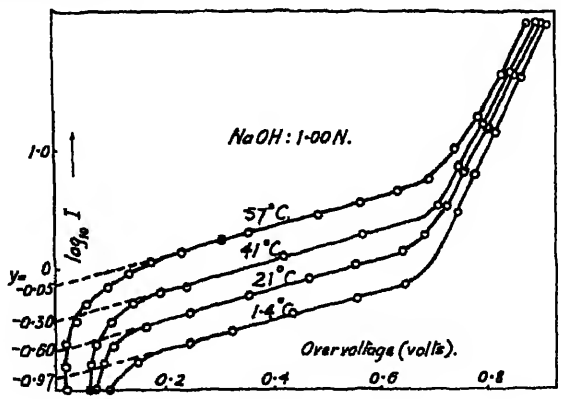


FIG. 6.

The numerical results are given in Table IA.

Fig. 8 relates to the anodic polarisation of Al, Ta and Mg; one can verify on the curves in Fig. 5, 6, 7 and 8 that the calculated points fall very exactly on the experimental curves.

2. As regards cathodic phenomena several cases may be considered. If the cathode is a solid metal or a two-phase amalgam, the theory only correctly applies for concentrations above 1/3 N.; $(\alpha + \beta) < 1$. For weaker concentrations, $\alpha + \beta$ is found to be greater than unity; the values

of α being always smaller than unity. It transpires further that the function $y = \frac{(\alpha + \beta)F\eta}{RT}$ does not vary linearly in the whole range of overvoltage as the theory requires ; it shows a "curving-in" for small overvoltages.

The sum of these facts leads to the supposition that the term corresponding to the ionisation process is not correctly expressed.

3. In the case of mercury and of a one-phase amalgam, eqn. (3) is, however, verified equally well for concentrated as for dilute solutions.

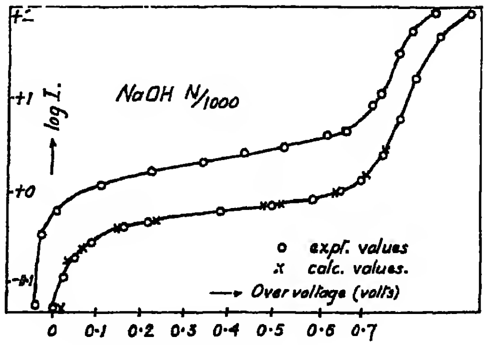


FIG. 7.

TABLE IA.

Electrolyte.	Temperature °C.	α.	$\alpha+\beta$.	γ_0.	α'.	γ_0'
			Anodic Polarisation.			
NaOH ; 1 N.	57·0	0·124	0·664	−0·05	−0·617	−4·89
	41·0	0·120	0·636	−0·30	−0·584	−4·94
	21·0	0·118	0·457	−0·60	−0·531	−4·99
	1·4	0·115	0·349	−0·97	−0·490	−5·06
NaOH : 0·001 N	56·5	0·063	0·300	0·20	—	—
	20·0	0·035	0·248	−0·26	—	—
NaN_3 ; 1 N.	57·0	0·135	0·313	0·34	1·108	−7·67
	42·0	0·142	0·363	−0·08	1·050	−8·00
	20·0	0·129	0·359	−0·64	0·965	−8·36
	1·4	0·117	—	−1·32	0·882	−8·8

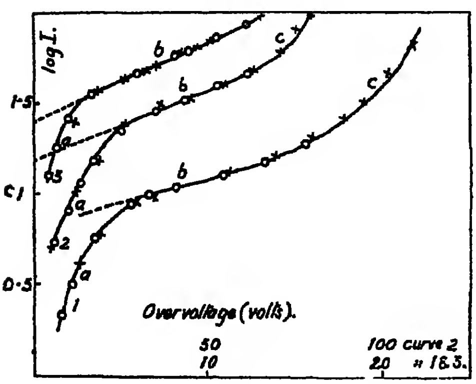


FIG. 8.

TABLE IB.

Electrolyte.	$\alpha+\beta$.	γ_0.
	Cathodic Polarisation.	
$NiSO_4$; 1 N.	25	0·0527
	95	0·212
$NiCl_2$; 1 N.	25	0·090
	95	0·212
$CoCl_2$; 1 N.	1	0·290
0·05 % boric acid	75	0·407
$CoCl_2$; 1 N.	50	0·426
	75	0·405
$CoSO_4$; 1 N.	1	0·221
	20	0·241
	75	0·250
$CoSO_4$; 1 N. 0·5 % boric acid.	1	0·232
	20	0·220
	50	0·250

These conclusions means that, in certain cases, the structure of the electrode itself may play an important role in the mechanism of the discharge. It is difficult to define this structure-factor, it will be seen later how the form of curves of potential energy allows the interpretation of

this influence; but one may already visualise this action, of the role of the active centres in the process of discharge, a role which has been indicated by certain authors and principally by Haissinsky.[1]

Be this as it may, it must further be remarked that in the conditions where the theory is applicable, the values of $\alpha + \beta$ found experimentally are often considerably smaller than unity. Now the identification of eqn. (3) for $I = 0$ with the thermodynamic expression of the potential, postulates essentially that $\alpha + \beta = 1$. We will find later the explanation of this fact.

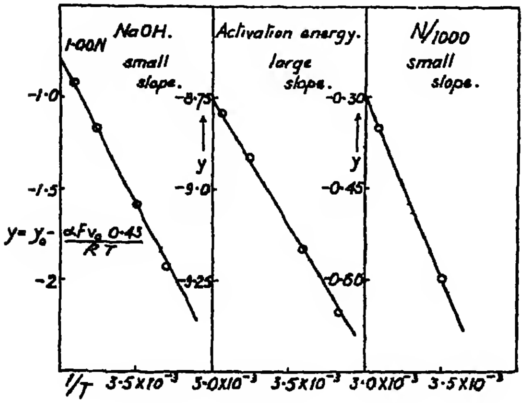


FIG. 9.

Determination of the Activation Energies.

The influence of temperature on the behaviour of the overvoltage curves offers a way of determining the relative values of activation energies. Neglecting the ionisation processes, we have

$$\log I = \log k[M^+] - \frac{w}{RT} + \frac{\alpha F V_0}{RT} + \frac{\alpha F \eta}{RT} \quad . \quad . \quad (4)$$

Writing γ_0 for the ordinate of the point where the linear part cuts the ordinate axis, we have

$$\gamma_0 = \log k[M^+] - \frac{w}{RT} + \frac{\alpha F \eta}{RT} \quad . \quad . \quad . \quad (5)$$

TABLE II

Ion.	Solution.	w_1.	w_2.
$\overline{N}_3$	NaN_3; 1 N.	12700 cal.	5800 cal.
$\overline{O}H$	NaOH; 1 N.	8300 ,,	3800 ,,
$\overline{O}H$	NaOH; 0·001 N.	3100 ,,	—
Co^{++}	$CoCl_2$; 1 N.	14250 ,,	—
Co^{++}	$CoSO_4$; 1 N.	14300 ,,	—
Co^{++}	$CoSO_4$; 1 N. + 0·003 N. H_2SO_4	14200 ,,	—
Amalgam 1-phase.			
Cu^{++}	$Cu(NO_3)_2$; various concentrations	5200 ,,	—
Hg_2^{++}	Nitrate solution; various concentrations	12000 ,,	—
Hg^{++}	Nitrate solution; various concentrations	5820 ,,	—

Thus it follows, that if one plots as abscissa $1/T$ and as ordinate the corresponding values of $y = \gamma_0 - \frac{\alpha F V_0}{RT}$, one has, even as experiment demonstrates, straight lines of which the slope permits calculation of w. The

[1] Haissinsky, *J. Chim. Physique*, 1946, 43, 21.

values given in the table have been obtained taking the value 0·54 V. for the Hg_2Cl_2-normal KCl *reference* electrode used.

Potential-energy Curves.

The deeper significance of the transmission factors of kinetic energy is difficult to define. But one may, by generalising the considerations given by Polanyi,[3] connect them with the potential-energy curves of the ion. We shall see that the form of these curves, furnishes a rational explanation of the experimental facts which have appeared.

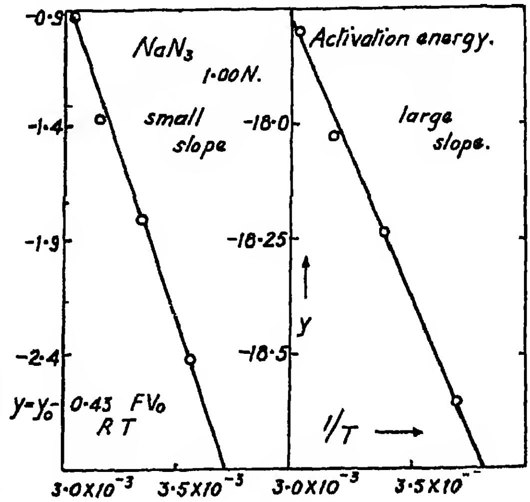


FIG. 10.

In Fig. 11, curve 1, the distance of the ion M (unsolvated) from the electrode is plotted as abscissa and the potential energy of the combination of the dehydrated ion with the metal M of the electrode as ordinate; the abscissa of the minimum value of this curve gives the stable position of the system. There is reason to think, being given that the ion finds itself in this state and incorporated in the superficial layer of the crystalline lattice of the metal, that d_0 is very small; in these conditions, one may admit that the corresponding potential is identified with the potential of the electrode.

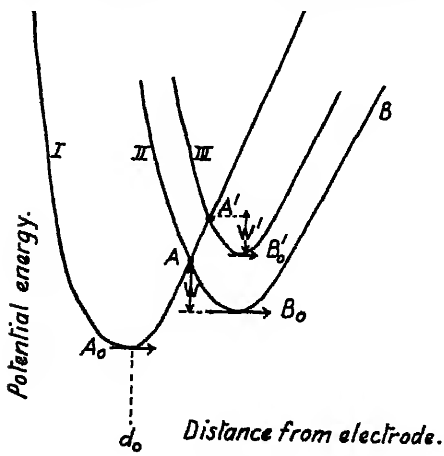


FIG. 11.

Curve II relates to the variation of the potential energy of the hydrated ion, M^+ aq.

In the absence of all overvoltage, the energy path of the process of discharge is thus shown as BB_0, AA_0; the relevant activation energy is w. Under the influence of an overvoltage η, the curve is displaced by translation a distance $B_0B_0' = \eta\epsilon$, where ϵ is the electronic charge, the activation energy then becoming w'. By assuming that in the region between the points A and A′, the curves remain approximately linear and parallel, it is easy to show by elementary geometrical considerations that

$$w' = w - \epsilon\eta(1 - \mu) \text{ with } \mu < 1.$$

In these conditions, one thus again finds the equation $w' = w - \alpha\epsilon\eta$

[3] Polanyi, *Acta Physicochim.*, 1935, **2**, 505.

where α is < 1 and independent of the overvoltage. This is a result which experiment in general confirms.

But as Bonnemay has remarked, it is more rational to consider from this point of view the more general problem ot the relative positions and form of the potential energy curves. Without seeking a complete solution, interesting results are, however, obtained, as we shall show, which interpret the experimental results better than the previous considerations, which are only approximate.

Curves I, II and III of Fig. 12 correspond respectively to an unhydrated on, a hydrated ion and finally to the latter in the case where overvoltage s present.

Consider a very small overvoltage $IJ = \epsilon\eta$. Curve III is deduced from curve II by simple translation; I thus becomes I′. If we now take two co-ordinate axes of origin I, the curve III cuts the axis Iy at J such that $IJ = \epsilon\eta$. By reason of the fact that $\epsilon\eta$ is very small I′J and II′ may be treated as straight lines. The straight line II′ is thus represented by $y = ax$ and the line I′J by $y = bx + \epsilon\eta$, $a = f(x)_I$ and $b = \phi(x)_I$ being

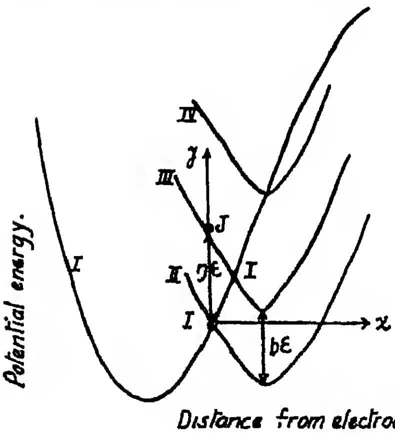


FIG. 12.

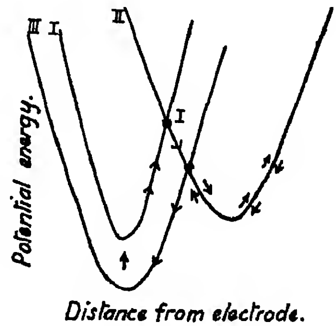


FIG. 13.

the slope of the energy-distance curves at the point I. The ordinate of the point I′ is thus $Iy = \dfrac{\epsilon\eta}{1 - \dfrac{b}{a}} = \beta\epsilon\eta$ from which one concludes:

$$\beta = \frac{1}{1 - \dfrac{b}{a}}; \quad \alpha = 1 - \frac{1}{1 - \dfrac{b}{a}}.$$

These two latter equations permit us therefore to see in a precise manner, how the coefficients α and β vary as a function of the slope of the two curves from their point of intersection, slopes which depend closely on the respective forms and positions of the potential energy curves. Thus, for example, when the curve for discharge of a hydrated ion occupies the position IV, the slope is very s'ight; $\phi'(x) \rightarrow 0$ and thus $\alpha \rightarrow 0$.

The activation energy of the process of discharge of the ion is then in the neighbourhood of zero; all ions having access to the electrode are discharged, the curve $\log I = f(\eta)$ then shows an abrupt diversion as one observes for high overvoltage in certain cases (H^+, for example).

In short, the constant $(\alpha + \beta)$ observed experimentally, in an extended range of overvoltage and in many cases will be correlated to the practically linear form of the curves of potential energy in this same range. Perhaps this is the place to interpret the second slope of α, steeper than the first,

and observed in certain experiments as connected with the steepness of curve II towards IV. But then if one so attains the position IV, the activation energy will not tend to be constant in this last range where it will tend to approach zero. But when the second slope of α is well defined as well as the second activation energy, one may attribute this fact to the existence of a different process of discharge (secondary reaction, alteration of the surface of the electrode, etc.). Be this as it may these considerations permit the elucidation of the mechanism of ionisation, and thus furnish the explanation of the very small values of $\alpha + \beta$ often found.

In a general manner, if one considers the two systems, hydrated ions—metal, and unhydrated ions—metal, all variations of energy from one to the other may be depicted by a displacement of the corresponding curve along the potential axis; the magnitude of the displacement being proportional to the variation of energy considered. Supposing that curve II remains fixed (e.g. at constant current density) the lower that curve I is the lower will be the energy of discharge. *The discharge thus occurs by preference on the areas of the cathode for which curve I is lowest, as a consequence of the heterogenity (always possible) of the electrode.*

If now under the same conditions we examine the ionisation energy, w', we see that the higher is curve I the lower is this quantity. *Ionisation therefore occurs by preference on the regions of the electrode which correspond to the highest position of curve I.* In other words the energy course followed by the discharge will be different from that followed at the time of ionisation (Fig. 13).

It results from this that the experimental calculation (coefficient of transfer appropriate at the time of the process of discharge) has to be made at the start of the slopes I and II on I, whilst that of β must be made at the commencement of the same heights on I'; but $\beta'_I < \beta_I$ since $\phi'_I < \phi_I$ and $f'_I < f_I$. It therefore results $\alpha_I + \beta'_I < \alpha_I + \beta_I$; as $\alpha_I + \beta_I = 1$, $\alpha_I + \beta'_I < 1$. These considerations thus well explain the reasons why one finds, as experiment indeed confirms, that in numerous cases the sum of the coefficients of transfer experimentally measured is less than unity.

Conclusions.—A careful examination of the potential-energy curves allows of a better comprehension of the physical meaning of the results obtained in the experimental study of the phenomena of overvoltage. In its most general form the problem of the discharge of ions on an electrode may be arrived at in the following manner.[4] Considering the curve of the system, unhydrated ion-electrode, for which the minimum energy is comprised between E and $E + dE$, the number of these combinations is $\Phi(E)dE$, $\Phi(E)$ designating the function of distribution. In an analogous manner, by considering the curve of the system, hydrated ion-electrode, for which the minimum energy is comprised between E' and $E' + dE'$ the number of these combinations is $\psi(E')dE'$; $\psi(E')$ being the function of distribution. Each centre of discharge being constituted by the total of energy passages of the two curves, their number is then equal to $\Phi(E) . \psi(E')dE . dE'$. The activation energy which corresponds to one of these passages is

$$w_1 = w_0 - \alpha(E' - E), \ \alpha < 1.$$

Under these conditions the number of ions which discharge is

$$k\,e^{\frac{w_0 - \alpha(E - E)}{RT}}.$$

But taking account of the overvoltage $w = w_1 - \alpha F\eta$ the discharge current of the assembly of all the ions is

$$I_{\text{discharge}} = k \int_0^{\infty} \int_0^{\infty} \Phi(E)\psi(E')\,e^{\frac{w_0 \quad \alpha(E' - E) - \alpha F\eta}{RT}}\,dE \,.\, dE'. \quad . \quad (7)$$

[4] Bonnemay, *Compt. rend.*, 1946, **223**, 76.

At the same time the ionisation current is

$$I_{\text{ion}} = k' \int_0^\infty \int_0^\infty \Phi(E)\psi(E')\, e^{\frac{w_0 + \beta(E' - E) + \beta F\eta}{RT}} \mathrm{d}E \, . \, \mathrm{d}E'. \qquad (8)$$

The total current is therefore

$$I = I_{\text{discharge}} - I_{\text{ion}} \qquad . \quad . \quad . \quad . \quad (9)$$

This general expression simplifies itself when one assumes that α and β are independent of the relative positions of the potential energy curves; in this case the sole variable is then the overvoltage and one obtains eqn. (3) given at the beginning of this paper, viz.,

$$I = A\, e^{\frac{\alpha F\eta}{RT}} - B\, e^{\frac{\beta F\eta}{RT}}.$$

A and B representing the double sums of eqn. (9).

In summary, these experimental results, as well as considerations based on the respective positions of the potential energy curves suggests that the theory of overvoltage is verified by supposing that α and β may not be constant over all the range of the overvoltage. In a number of other experimental cases, experiment shows that α and β may be considered as independent of η. Finally it is necessary in the case of discharges on a solid metallic electrode to make allowance for the existence of a structural factor.

Résumé.

Le mécanisme de la décharge des ions sur les électrodes est souvent fort complexe, mais en faisant intervenir l'énergie d'activation des ions dans la cinétique de l'électrolyse et en tenant compte des processus d'ionisation des produits de la décharge on obtient une relation représentant la variation de l'intensité en fonction du potentiel qui est vérifiée par l'expérience dans un très grand domaine du potentiel.

La théorie ainsi développée permet de déterminer les énergies d'activation des différents processus ; elle révèle en outre le mécanisme complexe de toute décharge.

En construisant des courbes d'énergie potentielle de l'ion, par rapport à l'électrode, on apporte des données supplémentaires à la connaissance de ce mécanisme et c'est ainsi que ces courbes mettent en évidence le rôle des centres actifs et fournissent des données interprétant les cas où la théorie élémentaire de l'énergie d'activation ne semble pas entièrement satisfaite.

Zusammenfassung.

Der Mechanismus der Abscheidung von Ionen an Elektroden ist oft sehr komplex, aber wenn die Aktivierungsenergien der Ionen in der Kinetik der Elektrolyse sowie die Ionisierungsvorgänge der Abscheidungsprodukte berücksichtigt werden, erhält man eine Relation, die die Veränderung der Stromdichte als Funktion des Potentials ausdrückt und die für ein grosses Potentialbereich experimentelle Bestätigung findet. Die entwickelte Theorie gestattet die Bestimmung der Aktivierungsenergien der verschiedenen Vorgänge und enthüllt auch den komplexen Mechanismus des ganzen Abscheidungsvorgangs. Bei der Konstruktion der potentiellen Energiekurven der Ionen mit Bezug auf die Elektrode werden die zusätzlichen Daten, die über den Mechanismus bekannt sind, benützt und auf diese Weise geben die Kurven Information über die Rolle der aktiven Zentren und liefern Daten zur Erklärung der Fälle, wo die einfache Theorie der Aktivierungsenergie nicht ganz befriedigend zu sein scheint.

THE INTERPRETATION OF OVERPOTENTIAL MEASUREMENTS.

By J. N. Agar.

Received 14th March, 1947.

The rate of an electrode reaction depends on a variable—the electrode potential—that does not appear in other branches of chemical kinetics. But this fact does not justify the tendency, apparent in much of the published work on electrode reactions, to study only the relation between current and potential and to neglect other variables. By analogy with ordinary chemical kinetics, one might suppose that the investigation of the influence of temperature and of concentration of reactants and of neutral salts would prove valuable, and it is regrettable that so little attention has been paid to these factors in experimental work on activation overpotential.[1]

An attempt is made in this note to indicate the kind of information which can be obtained from measurements of the temperature coefficient of overpotential, and from observations of the influence of concentration of reactants and neutral salts.

The Influence of Temperature on Overpotential.

(1) The Heat of Activation.—Two different techniques may be used to study the kinetics of electrode reactions at varying temperatures,

I. The overpotential, η, at any temperature T is measured against a reversible electrode at the same temperature T.

II. The potential, V, of the working electrode at the variable temperature T is measured against a standard electrode kept at a fixed temperature, T_0. Some uncertainty is introduced into the results by thermo-electric potentials arising in the tube connecting the cell at temperature T to the standard electrode at T_0.

Two slightly different heats of activation, E_{I} and E_{II}, corresponding to the two methods of measurement, may be defined :

$$\left(\frac{\partial \ln i}{\partial T}\right)_\eta = \frac{E_{\mathrm{I}}}{RT^2} \qquad . \quad . \quad . \quad . \quad (1)$$

$$\left(\frac{\partial \ln i}{\partial T}\right)_V = \frac{E_{\mathrm{II}}}{RT^2} \qquad . \quad . \quad . \quad . \quad (2)$$

where i is the current density. In general, both E_{I} and E_{II} depend on the potential.

Since

$$\frac{d \ln i}{dT} = \left(\frac{\partial \ln i}{\partial T}\right)_\eta + \left(\frac{\partial \ln i}{\partial \eta}\right) \cdot \frac{d\eta}{dT} \qquad . \quad . \quad . \quad (3)$$

the temperature coefficient of overpotential at constant current density is :[2]

$$\left(\frac{\partial \eta}{\partial T}\right)_i = -\frac{E_{\mathrm{I}}}{RT^2} \Big/ \left(\frac{\partial \ln i}{\partial \eta}\right)_T \qquad . \quad . \quad . \quad (4)$$

and if the relation between $\ln i$ and η is written in the form :

$$\ln i = \ln i_0 + \frac{\alpha F \eta}{RT} \qquad . \quad . \quad . \quad . \quad (5)$$

[1] Bowden and Agar, *Ann. Reports*, 1938, 35, 90.
[2] Stout, *Trans. Faraday Soc.*, 1945, 41, 64.

we have

$$\left(\frac{\partial \ln i}{\partial \eta}\right)_T = \left(\frac{\partial \ln i}{\partial V}\right)_T = \frac{\alpha F}{RT} \quad . \quad . \quad . \quad (6)$$

and hence

$$\left(\frac{\partial \eta}{\partial T}\right)_i = -\frac{E_{\mathrm{I}}}{\alpha F T} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By a similar argument

$$\left(\frac{\partial V}{\partial T}\right)_i = -\frac{E_{\mathrm{II}}}{\alpha F T} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Equations (3), (4), (7) and (8) are perfectly general, and do not require E or α to be constant.

If V_0 is the potential of the reversible electrode at T against the standard electrode at T_0, we have

$$\eta = V - V_0$$

and

$$\left(\frac{\partial \eta}{\partial T}\right)_i = \left(\frac{\partial V}{\partial T}\right)_i - \left(\frac{\partial V_0}{\partial T}\right)$$

whence

$$E_{\mathrm{I}} - E_{\mathrm{II}} = \alpha F T \frac{\partial V_0}{\partial T} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Taking $\alpha = 0{\cdot}5$, $T = 300°$ K. and $\partial V_0/\partial T = \pm\, 0{\cdot}5$ mv. per °C., as typical values, the difference between E_{I} and E_{II} is found to be approximately 1·7 kcal. Most of the published values of energies of activation [1, 2] are those of E_{II}.

(2) **Relation between Heat of Activation and Potential.**—For the discharge of hydrogen ions from 0·2 N sulphuric acid at a mercury cathode, Bowden [3] showed that the same value of E_{II} was obtained by using equations (2) and (8). He also found that α had the same value (0·5) at all the temperatures investigated, and that the variation of E_{II} with the potential of the cathode, V, was given by:

$$E_{\mathrm{II}} = W - \alpha F V \quad . \quad . \quad . \quad . \quad (10)$$

W being a constant. These results have since been confirmed by Kenyon.[4]

Equation (10) is very easily derived on the assumption that overpotential is due to the slow discharge of hydrogen ions,[5] the height of the energy barrier over which the reacting system must pass being directly affected by the metal-solution potential difference. It does not seem to be so clearly recognised that a relation of the same form can also be derived by assuming other mechanisms, in which the potential has no *direct* effect on the height of the energy barrier.

Consider, for example, the simple "Tafel" recombination mechanism,[6] according to which the slow stage in the electrode reaction is the combination of adsorbed H atoms to form H_2 molecules. It is assumed that the adsorbed atoms are in equilibrium with the solution and occupy only a *small* fraction, θ, of the available sites. We then have:

$$i = k\theta^2$$

$$\eta = \frac{RT}{F}\ln\frac{\theta}{\theta_0}$$

whence

$$\ln i = \ln i_0 + \frac{2F}{RT}\eta \quad . \quad . \quad . \quad . \quad (11)$$

where k is a constant, θ_0 is the fraction of the surface occupied at the reversible potential (i.e., in equilibrium with hydrogen gas) and $i_0 = k\theta_0^2$

[3] Bowden, *Proc. Roy. Soc. A*, 1929, **126**, 107.
[4] Kenyon (private communication).
[5] Volmer and Erdey-Gruz, *Z. physik. Chem. A*, 1930, **150**, 203. Horiuti and Polanyi, *Acta Physicochim.* 1935, **2**, 505. Butler, *Proc. Roy. Soc. A*, 1936, **157**, 423.
[6] e.g. Knorr and Schwartz, *Z. Elektrochem.*, 1934, **40**, 38.

is the rate of dissociation of H_2 or of recombination of adsorbed atoms at the reversible potential.

It follows that

$$\frac{E_I}{RT^2} = \left(\frac{\partial \ln i}{\partial T}\right)_\eta = \left(\frac{\partial \ln i_0}{\partial T}\right) - \frac{2F\eta}{RT^2}$$

or

$$E_I = W_0 - 2F\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where $W_0 = RT^2 \frac{\partial \ln i_0}{\partial T}$. Apart from the numerical value of α, this relation has the same form as (10); it may readily be transformed into a relation between E_{II} and V.

The actual values of E_I and E_{II}, and, in particular, their values at the reversible potential, are of more significance in elucidating the mechanism of overpotential. For example, the observed value of E_{II} for hydrogen deposition from acid solution on mercury is 18 kcal. per g. ion at the reversible potential,[1] and this shows immediately that the formation of free atomic hydrogen is highly improbable. The calculation of entropies of activation, or equivalent "temperature independent" factors [7] is also a matter of considerable interest.

(3) **Variation of α with Temperature.**—Although α is independent of temperature under the conditions of Bowden's experiments, a definite variation of α with temperature has been found in certain other reactions. The observations of Stout [2] on the deposition of the azide ion and of Roiter and Jampolskaja [8] on the electro-reduction of oxygen are especially interesting; the usual linear relation between V and $\log i$ is found, but the slope, b, of the $V - \log i$ lines is nearly independent of temperature.

Since

$$\alpha = \frac{2{\cdot}303\, RT}{bF}, \quad \text{(cf. (5))} \quad . \quad . \quad . \quad . \quad (13)$$

it follows that α is proportional to the absolute temperature. Furthermore, since the $V - \log i$ lines at different temperatures are parallel to one another, the heat of activation,

$$E_{II} = RT^2 \left(\frac{\partial \ln i}{\partial T}\right) ,$$

is independent of potential. It is difficult to explain this result, or, indeed, any appreciable variation of α with temperature, in terms of an ion-discharge mechanism alone. Formally, however, an E independent of V and an α proportional to T can be obtained by assuming that the potential affects not the *heat*, $\Delta H^{\ddagger}$, but only the *entropy*, $\Delta S^{\ddagger}$, of activation. If we put:

$$\left(\frac{\partial \Delta S^{\ddagger}}{\partial V}\right)_T = \beta F = constant; \quad \left(\frac{\partial \Delta H^{\ddagger}}{\partial V}\right)_T = 0,$$

we obtain [9]

$$\frac{\alpha F}{RT} = \left(\frac{\partial \ln i}{\partial V}\right)_T = -\frac{1}{RT}\left(\frac{\partial \Delta F^{\ddagger}}{\partial V}\right)_T \quad . \quad . \quad . \quad (14)$$

$$= -\frac{1}{RT}\left(\frac{\partial \Delta H^{\ddagger}}{\partial V}\right)_T + \frac{1}{R}\left(\frac{\partial \Delta S^{\ddagger}}{\partial V}\right)_T = \frac{\beta F}{R}$$

or

$$\alpha = \beta T.$$

It is probable, however, that variation of α with temperature really implies that the reaction is complex, or that factors such as adsorption

[7] Eyring, Glasstone and Laidler, *J. Chem. Physics*, 1939, **7**, 1053. Glasstone, Laidler and Eyring, *The Theory of Rate Processes* (1941), ch. 10. Kimball, Glasstone and Glassner, *J. Chem. Physics*, 1941, **9**, 91.

[8] Roiter and Jampolskaja, *Acta Physicochim.*, 1937, **7**, 247.

[9] Cf. Eyring, Glasstone and Laidler,[7].

have to be explicitly considered,[10] and a much more detailed analysis is required in order to see the true significance of the experimental results.

The Influence of Concentration of Reactants and Neutral Salts.

If the rate-controlling process involves only adsorbed atoms, it is reasonable to suppose that the *overpotential* at a given current density will be practically independent of the concentrations of reacting ions and of neutral salts, although the total metal-solution potential difference at an electrode where reaction is occurring, and at a reversible electrode, depends on these concentrations.

On the other hand, if the rate-controlling stage involves neutralisation or formation of an ion, it is to be expected that addition of neutral salts and changes in the concentration of the reactant in the solution will affect the overpotential. But, as Frumkin [11, 12] has shown, the situation is complicated by the existence of the potential ϕ_g associated with the diffuse (Gouy) part of the double-layer and by the related adsorption of reacting ions. Frumkin [11] has considered the discharge of hydrogen ions on mercury in terms of the Stern theory of the double layer; although this theory does not explain all the observations quantitatively, it does account for some of the more puzzling features, and a treatment on similar lines should certainly be applied to other reactions for which similar mechanisms are postulated.

The assumptions made by Frumkin are:

(i) the total metal-solution potential difference * ϕ is made up of two parts—ϕ_h across the Helmholtz double layer and ϕ_g across the diffuse double layer;

(ii) the rate of discharge of ions is [13]

$$i = k[H^+]_s \, e^{\frac{\alpha F \phi_h}{RT}} \quad . \quad . \quad . \quad . \quad (15)$$

where $[H^+]_s$ is the concentration on the solution side of the Helmholtz double layer;

(iii) $[H^+]_s$ is related to the bulk concentration $[H^+]_0$ by the equation:

$$[H^+]_s = [H^+]_0 \, e^{\frac{F\phi_g}{RT}}. \quad . \quad . \quad . \quad . \quad (16)$$

It follows that

$$\phi = \frac{RT}{\alpha F} \ln i - \frac{RT}{\alpha F} \ln [H^+]_0 - \left(\frac{1-\alpha}{\alpha}\right)\phi_g + const. \quad . \quad (17)$$

and, introducing the reversible potential, $\phi_0 = const. - \frac{RT}{F} \ln [H^+]_0$:

$$\eta = \phi - \phi_0 = \frac{RT}{\alpha F} \ln i - \left(\frac{1-\alpha}{\alpha}\right) \frac{RT}{F} \ln [H^+]_0 - \left(\frac{1-\alpha}{\alpha}\right)\phi_g + const. \quad (18)$$

At constant i and $[H^+]_0$ and for $\alpha < 1$, η should thus be increased by adding neutral salts, which usually decrease ϕ_g; salts with specifically adsorbed anions (e.g. iodides) may increase ϕ_g and thus decrease η. Qualitatively, these conclusions have been confirmed by experiment.[13, 14]

In the presence of excess neutral salt, ϕ_g should be approximately

* ϕ is taken to be zero in the metal; Frumkin uses the opposite sign convention.

[10] Jofa and Stepanov, *J. Physic. Chem.* (*Russ.*), 1945, 19, 125; *Chem. Abs.*, 1945, 4011.

[11] Frumkin, *Z. physik. Chem.*, *A*, 1933, 164, 121.

[12] Frumkin, *Acta Physicochim.*, 1943, 18, 23 (this paper contains numerous references to earlier work).

[13] Cf. Volmer and Erdey-Gruz,[5].

[14] Jofa, Kabanov, Kuchinski and Chistyakov, *Acta Physicochim.*, 1939, 10, 317. Frumkin, *Trans. Faraday Soc.*, 1940, 36, 126.

constant and independent of $[H^+]_0$; η should therefore increase as the hydrogen ion concentration is lowered. Lewina and Sarinsky [15] observed a change of η in the expected direction in solutions of varying $[H^+]_0$ containing $LaCl_3$, but other investigators have found η practically independent of $[H^+]_0$ under analogous conditions (e.g. Bowden,[16] using buffer mixtures; Wagner and Traud,[17] using solutions of composition 1 M $CaCl_2$, $(1 - x)$ M KCl, x M HCl). Further experimental work on this point seems to be called for.

In acid solutions containing no neutral salts, ϕ_g changes with $[H^+]_0$, and, for mercury at potentials in the usual experimental range of hydrogen overpotentials, Frumkin calculates from Stern's theory that

$$\phi_g = const. - \frac{RT}{F} \ln [H^+]_0$$

approximately. Hence, using (18) and putting $\alpha = 0{\cdot}5$, we obtain:

$$\eta = \frac{2RT}{F} \ln i + const. \qquad (19)$$

The overpotential is thus independent of $[H^+]_0$, as found experimentally in dilute solutions.

It should be noted that the effect of neutral salts is in the opposite sense if the reacting particle is a water molecule, as suggested by Eyring, Glasstone and Laidler,[7] instead of a hydrogen ion. We then have [18]

$$i = k[H_2O]\, e^{\frac{\alpha F\phi_h}{RT}} = k'\, e^{\frac{\alpha F\phi_h}{RT}} \qquad (20)$$

and

$$\phi = \phi_h + \phi_g = \frac{RT}{\alpha F} \ln i + \phi_g + const. \qquad (21)$$

$$\eta = \phi - \phi_0 = \frac{RT}{\alpha F} \ln i + \frac{RT}{F} \ln [H^+]_0 + \phi_g + const. \qquad (22)$$

the sign of ϕ_g being opposite to that in (18), provided $\alpha < 1$.

This example serves to show how the existence and sign of a neutral salt effect may discriminate between different mechanisms. But it must be emphasised that the Stern theory of the double layer is in many respects inadequate.[19] In particular, it takes no account of the lateral distribution of ions in the Helmholtz double layer, in consequence of which ϕ_g and ϕ_h vary from point to point of the surface, although their sum, ϕ, remains constant. If $\alpha < 1$, (17) shows that the current density for discharge of H^+ at a given overall ϕ is greatest at points where ϕ_g is greatest and ϕ_h least. It is clearly desirable that the theory of the double-layer should be developed so that effects of this type can be dealt with quantitatively.

I am indebted to Dr. F. P. Bowden and Dr. H. P. Stout for stimulating discussion of the subject matter of this paper.

Summary.

The influence of temperature and of concentration of reactants and neutral salts on overpotential is briefly discussed, and some of the possible implications of experimental results, in this field are indicated.

[15] Lewina and Sarinsky, *Acta Physicochim.*, 1937, **6**, 491; *ibid.*, 1937, **7**, 485.
[16] Bowden, *Trans. Faraday Soc.*, 1928, **24**, 473.
[17] Wagner and Traud, *Z. Elektrochem.*, 1938, **44**, 391.
[18] Cf. Lukowzew, Lewina and Frumkin, *Acta Physicochim.*, 1939, **11**, 21.
[19] Cf. Jofa and Frumkin, *ibid.*, 1943, **18**, 143.

Résumé.

On discute brièvement l'influence de la température et de la concentration en réactifs et en sels neutres sur le survoltage et on indique quelques unes des conséquences possibles impliquées par les résultats expérimentaux dans ce domaine, en ce qui concerne le mécanisme des réactions à l'électrode.

Zusammenfassung.

Der Einfluss von Temperatur und von Reagens- und Neutralsalzkonzentration auf die Überspannung wird kurz besprochen und es wird auf die mögliche Bedeutung von Versuchsresultaten auf diesem Gebiet für den Mechanismus von Elektrodenreaktionen hingewiesen.

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OVERPOTENTIAL AT VERY LOW CURRENT DENSITIES. THE DEPOSITION OF HYDROGEN FROM AQUEOUS AND NON-AQUEOUS ELECTROLYTES.*

BY F. P. BOWDEN AND K. E. W. GREW.

Received 11th March, 1947.

The fact that the electrodeposition of an ion can occur at an appreciable rate only when the potential between the electrode and the electrolyte exceeds the reversible potential—that is, the phenomenon of overpotential—implies that some stage of the process can only occur at a limited rate, which is dependent on the potential. This overpotential may be classified (Agar and Bowden, 1938, 1939) as *activation overpotential* V_a if the slow process requires an energy of activation, as *concentration overpotential* V_c if it is due to concentration changes in the electrolyte near the electrode, and as *resistance overpotential* V_r if it is caused by a high resistance at the electrode surface.

Earlier work has shown that for the deposition of hydrogen on most metals, the velocity-controlling process could be regarded as one in which an energy of activation W was required. It was suggested (Bowden, 1929) that the effect of the potential difference V across the metal/electrolyte interface is to cause an alteration in this energy of activation by an amount proportional to V, so that the new energy of activation is $W - \alpha VF$. If the distribution of energy among the reacting species is Maxwellian, the number reacting per sec. N is given by

$$N = N_0 e^{-\frac{(W - \alpha VF)}{RT}} \quad . \quad . \quad . \quad . \quad (1)$$

where N_0 is the number present at the electrode surface. If N is measured by the current density i,

$$\ln i = const - \frac{\alpha F}{RT} . V \quad . \quad . \quad . \quad . \quad (2)$$

This may be written in the form

$$V = b (\log i - \log i_0) \quad . \quad . \quad . \quad . \quad (3)$$

* This work was carried out in 1936 (Grew, *Ph.D. Thesis*, (Camb. 1936), but publication and discussion of the results was interrupted by the war. This paper gives a brief outline of some of the experimental observations.

where $b = 2{\cdot}303RT/\alpha F$ and i_0 is the rate of deposition of hydrogen ions at the reversible potential. At this potential, the deposition of hydrogen is exactly balanced by the reverse process, the electrosolution of hydrogen, so that the net rate of deposition is zero. At other potentials, the observed c.d. is actually equal to the difference between the rate of deposition and the rate of electrosolution. The rate of electrosolution is usually negligibly small compared to the rate of deposition when the overpotential exceeds about 0·05 v., so that, after this, the overpotential should increase linearly with log (c.d.). As early as 1905, Tafel showed experimentally that, over a limited range of c.d., this logarithmic relation was approximately true for the deposition of hydrogen from acid solutions. It has been shown in earlier papers [1, 2, 3] that, provided certain precautions are taken, the logarithmic relation holds very accurately over a wide range of c.d. for both oxygen and hydrogen deposited from acid or alkaline solutions on to the surface of a large number of metals. The values of the constants may change with the conditions, but the logarithmic relation still holds. In the case of hydrogen, this was true for a range of c.d. extending from 10^{-2} to 10^{-7} amp./cm.^{2}. At c.d. above 10^{-2} amp., the overpotential rose sharply above the theoretical value. This is due to the fact that the high c.d. decreases the concentration of hydrogen ions in the immediate vicinity of the cathode. This changes the reversible potential of the electrode, and may also introduce a high resistance into the circuit, so that both V_c and V_r become appreciable. If the electrolyte is vigorously stirred so that these concentration changes are diminished, higher c.d. may be used before this break occurs.

In the earlier work, it was not possible to measure the overpotential of hydrogen at c.d. smaller than 10^{-7} amp./cm.^{2} because the overpotential became unsteady and *fell below* the theoretical value. It was suggested that this falling-away was caused by the presence in the electrolyte of small traces of oxygen, or oxidising substances, or metal ions which "depolarised" the electrode. The object of the present work was to extend the range of experimental observation down to very low c.d. An attempt has been made to eliminate these minute traces of oxidising substances and to determine whether the overpotential follows the same course down to very low c.d. or whether some other stage of the deposition process may play a part when the reaction velocity becomes very slow.

A mercury cathode was used, and the mercury and the electrolyte were distilled into a glass vessel which had previously been baked out in a high vacuum and filled with pure hydrogen. The vessel was then sealed off and the polarising current was passed, and the potential measured *through glass walls*. In this way, the cathode and the electrolyte surrounding it was protected from contamination by oxygen or other external impurities. The method was effective, and accurate measurements were obtained at c.d. as low as 10^{-9} or 10^{-10} amp./cm.^{2}

An investigation of overpotential in non-aqueous electrolytes is difficult under normal conditions because many of these have a high electrical resistance. This introduces a large ohmic potential drop into the circuit, so that V_r becomes very large. At these very low c.d., however, this ohmic drop becomes very small, so that accurate measurements of the overpotential are possible. The deposition of the hydrogen ion from methyl alcohol, pyridine and formic acid was investigated.

Results.

Deposition from N/5 Sulphuric Acid in Water.—The area of the mercury cathode in these experiments was 6 cm.^{2}. When the cell was

[1] Bowden and Rideal, *Proc. Roy. Soc. A*, 1928, **120**, 59.
[2] Bowden, *ibid.*, 1929, **125**, 446.
[3] *Ibid.*, 1929, **126**, 107.

freshly filled, the potential at low c.d. (less than 10^{-8} amp./cm.^{2}) was at first somewhat variable. After electrolysis for a short time, however, it reached a steady value. Eight distinct sets of measurements were made, the cell being emptied and refilled between each. The reproducibility was very good, and typical results taken from two different experiments are shown in Fig. 1. The overpotential in amp./cm.^{2} is plotted against the measured overpotential. The experiments show that the linear relation between the overpotential and the logarithm of the c.d. holds down to very low c.d. (10^{-9} amp./cm.^{2}). The slope of the line $dv/d \ln i$ is equal to 0·138 at 290° K. This is a mean value taken from four sets of measurements; it gives a value of $\alpha = 0{\cdot}45$ and it is not very different from that obtained at high c.d. At c.d. below 10^{-9} amp./cm.^{2}, the linear relation no longer holds, and the curve flattens out. Such an effect is to be expected at very small overpotentials, on account of the increasing importance of the back reaction. In the experimental curves, however, this flattening occurs at an appreciable overpotential and even on open circuit, the potential does not fall to zero. This suggests that a trace of some electronegative metal which may come from the glass itself, is deposited on the mercury. The value of i_0 obtained by extrapolation to zero overpotential is $i_0 = 4 \times 10^{-11}$ amp./cm.^{2}.

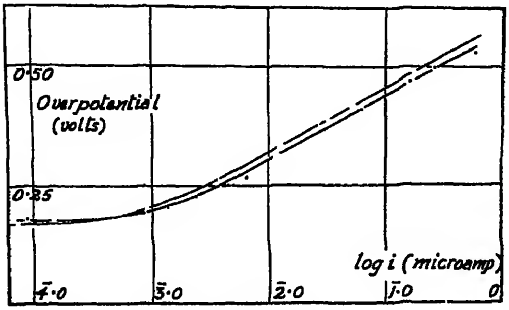

FIG. 1.

At the smallest c.d., a considerable time was required for the potential to become stationary. The electrode/electrolyte interface has a capacity of about 20 mfd./cm.^{2} (see later). Therefore a potential change of 100 mv. necessitates a change in the interfacial charge of 2 microcoulombs, and a current of 10^{-9} amp. must flow for 30 min. to bring this about. This meant that the full range of c.d. could not be covered in less than a few hours. No inconvenience arose from the extended duration of the measurements; the cell behaved consistently and reproducible results were obtained over a considerable period of time—in one case as long as 3 weeks.

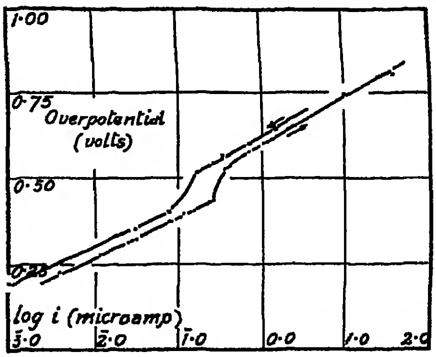

FIG. 2.

Deposition from Hydrochloric Acid in Methyl Alcohol.—A similar series of experiments were carried out using HCl dissolved in methyl alcohol. The alcohol was carefully purified and dried by successive distillation over NaOH and I_2, over CaO, over anhydrous $CuSO_4$ and an Al—Hg couple. The reference electrode was a reversible hydrogen electrode immersed in the same solution as that used in the cell. For measurements at the higher c.d., an internal anode was used, since the resistance of the glass bulb on the polarising circuit prevented measurements from being made with the external anode at c.d. greater than

10^{-6} amp./cm.^{2}. The internal anode was used only after the measurements at smaller currents were completed. Effects due to contamination of the solution by the products of electrolysis were thus minimised. Two sets of measurements were made, one for a 0·354 N. solution, and the other for a 0·14 N. solution of HCl. The results in both cases were similar and the curve obtained for the latter is shown in Fig. 2.

The curve shows that, except over a small range of c.d. (between 10^{-7} and 10^{-6} amp./cm.^{2}), the linear relation holds just as for aqueous solutions. There is indeed a close resemblance between the two cases. The slope $dV/d(\log i)$ of the curve for the alcohol solution is at the higher densities 0·14, at the lower 0·10; for the aqueous solutions, the average value found in these experiments was 0·14. Also the intercept on the axis of zero overpotential, which is a measure of the rate of the reversible reaction, is for the alcohol solution at $i_0 = 3 \cdot 10^{-11}$ amp./cm.^{2}, and for the aqueous solutions, $i_0 = 4 \cdot 10^{-11}$ amp./cm.^{2}.

The break in the $V - \log i$ curve showed a hysteresis effect, as is seen from the curves for increasing and decreasing currents. This suggests that there may be two types of ionic complex taking part. The presence of a trace of water in the alcohol might possibly account for this.

Hydrochloric Acid in Pyridine.—Experiments with pyridine as solvent are of interest because here the ionic complex is entirely different from that in water or alcohol solutions. The pyridine used was purified by distillation from KOH. The strength of the solution, determined at the end of the measurements by titration, was 0·04 N. HCl.

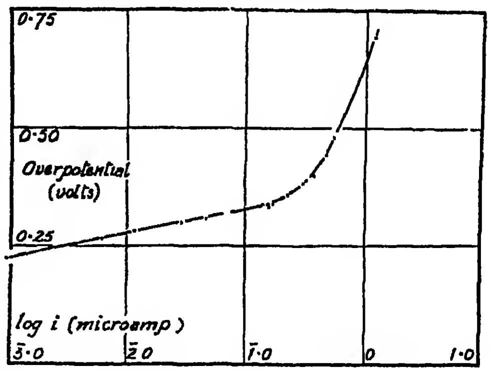

FIG. 3.

As reference electrode a calomel electrode was used. A reversible hydrogen electrode was set up in some of the residual solution and its potential measured, also with respect to the calomel electrode. The asymmetry potential across the glass bulb was measured and allowed for in calculating the overpotential values.

The first measurements made soon after filling the cell showed the linear relation between the potential and the logarithm of the current to hold over a range from 10^{-9} to 10^{-6} amp./cm.^{2}. The curve is given in Fig. 3. With continued polarisation over 24 hr., however, a break occurred in the curve, and potential readings became impossible because of uncontrollable fluctuations. This effect is possibly due to the accumulation of the products of a secondary reaction on the electrode surface.

The slope of the curve is much smaller than for aqueous or alcohol solutions, its value being only 0·05. The intercept on the axis of zero overpotential is also very different. The reversible current (of which the intercept is a measure) is $5 \cdot 10^{-11}$ amp./cm.^{2}; for alcohol and water solutions, the corresponding value is 4×10^{-11} and 3×10^{-11} amp./cm.^{2} respectively.

Formic Acid.—Pure formic acid is appreciably dissociated, and the conductivity is such that hydrogen deposition from it could be studied by this method without modification. The acid was prepared from lead formate and carefully dried by distillation from anhydrous $CuSO_4$.

Unfortunately, in this case no satisfactory value could be obtained or the reversible potential. The measurements are therefore given with

reference to a saturated calomel electrode, and are not overpotential values.

A typical curve is given in Fig. 4. Here again the logarithmic relation appears to be valid over a range from 10^{-8} to 10^{-6} amp./cm.^{2}. The change in slope at the smallest currents is similar to that observed in the case of the H_2SO_4 solutions. The slope $dV/d(\log i)$ is the smallest so far observed, being only 0·024.

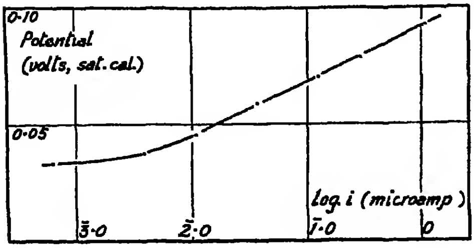

FIG. 4.

Discussion.

The results obtained for the deposition of the hydrogen ion from aqueous solution show clearly that the overpotential obeys equation (1) from c.d. of 10^{-6} amp./cm.^{2} down to c.d. as low as 10^{-9} or 10^{-10} amp./cm.^{2}. Moreover the slope of the line $dV/d(\log i)$ is equal to 0·138 or α (from equation (1)) is equal to 0·45. This value of α is only slightly lower than that observed at high c.d. Previous work has shown that the relation is obeyed at c.d. of 10^{-6} to 10^{-2} amp./cm.^{2} and that α equals *ca* 0·5. A c.d. of 10^{-10} corresponds to a deposition rate of 10^{-14} g. ions per sec., or *ca.* 6×10^{-7} atomic layers per sec., i.e. less than a millionth of an atomic layer per sec. Although the hydrogen ions are being deposited at this very low rate, the potential remains steady and the reaction velocity can be measured. It is clear that over this very great range of c.d. (10^{-10} to 10^{-2} amp./cm.^{2}) the reaction follows the same course.

The experiments in methyl alcohol, in pyridine and in formic acid show that the electrodeposition of the hydrogen ion from these electrolytes is again accompanied by an activation overpotential. Although the kinetics are similar, the values of α and of i_0 may be very different from those obtained in aqueous solution.

Résumé.

Le survoltage d'hydrogène a été mesuré à des densités de courant inférieures à 10^{-7} amp./cm^2. Les résultats, obtenus pour le dépôt d'ions hydrogène à partir de solutions aqueuses, montrent que les courbes $V - \log i$ ($\log i$) sont des droites (où V est la différence de potentiel à travers l'interface métal-électrolyte et i la densité de courant) et que la pente reste la même dans le domaine de densité de courant 10^{-10}-10^{2} amp./cm^2. Dans l'alcool méthylique, la pyridine et l'acide formique, la cinétique du dépôt est la même, mais les constantes des courbes $V = f(\log i)$ peuvent être différentes.

Zusammenfassung.

Die Wasserstoffüberspannung wurde bei Stromdichten unter 10^{-7} A/cm.^{2} gemessen. Die Resultate für die Wasserstoffabscheidung in wässerigen Lösungen zeigen, dass die Beziehung zwischen der Spannungsdifferenz (V) an der Phasengrenzfläche Metall-Elektrolyt und der Stromdichte (i) linear ist und dass die Steigung der V-log i-Linien im Stromdichtenbereich 10^{-10}-10^{-2} A/cm.^{2} unverändert bleibt. In Methylalkohol, Pyridin und Ameisensäure ist die Kinetik der Abscheidung ähnlich, aber die Konstanten der V-log i-Linien können sehr verschiedene Werte annehmen.

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AN EXPERIMENTAL DETERMINATION OF THE CAPACITY OF THE DOUBLE-LAYER.*

By F. P. Bowden and K. E. W. Grew.

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The development of a method for overpotential measurements at very small c.d. enables the capacity of the double-layer to be readily determined by direct measurement. When polarising currents of the order of 1 microamp. are used, the rate of charging up of the electrode/solution interface is so slow that it can conveniently be followed with a Compton electrometer. For instance, the time required for the potential at a mercury/sulphuric acid interface of 6 cm. area to change by 0·2 v. was 30 sec. when the current was 0·3 microamp. The method is applicable only over a small range of potential, the upper limit of which is determined by the rate of response of the electrometer.

Experimental.

When the glass cell had been filled and sealed, and the overpotential curve obtained, the polarising current was reduced to a very small value, i_1. The polarising E.M.F. and the resistance were so chosen that when a part of the resistance was short-circuited, the polarising current would increase to a value i_2 about 30 to 60 times greater than its initial value. The potential difference between the mercury electrode and the reference electrode was balanced on the potentiometer. The sensitivity of the potentiometer was now reduced, by changing the needle potential, to about one-third of its normal working value, which was 300 cm. per v. The reduced sensitivity was measured by disturbing the balance to a known extent. The resistance was now short-circuited, and the electrometer deflection observed at regular intervals—usually of 5 sec. duration—until a steady value was reached, corresponding to the overpotential appropriate to the larger current i_2. This current was then measured in the usual way.

From the curve showing the variation of the deflection θ with time t, the initial rate of deflection $\mathrm{d}\theta/\mathrm{d}t$ at time $t = 0$ was found. The corresponding initial rate of increase of potential $\mathrm{d}V'/\mathrm{d}t$ was calculated from this quantity and the sensitivity of the electrometer, and the capacity K from the relation:

$$K = -(i_2 - i_1)\Big/\left(\frac{\mathrm{d}V}{\mathrm{d}t}\right)_{t=0}.$$

In some cases the capacity was determined from the alternative expression

$$K = -\frac{\int_0^{\Delta t} i\,\mathrm{d}t}{\Delta V'}$$

in which i is the current serving to charge the interface, that is $(i_1 - \bar{\imath}_1)$, where $\bar{\imath}_1$ is the "leakage" current due to imperfect polarisability at any instant between 0 and Δt. This current $\bar{\imath}_1$ was found from an overpotential curve previously taken. The difference in the values of the capacity given by these two methods of calculation was not greater than the experimental error, and in general the results were calculated by the simpler method of the initial slope. In some cases the measurements were

* This work was carried out in 1936 (Grew, *Ph.D. Thesis*, Camb., 1936), but publication and discussion of the results was interrupted by the war. This paper gives a brief outline of some of the experimental observations.

extended to a higher range of potential by substituting for the electrometer an Einthoven galvanometer. The arrangement used was essentially that described in earlier work.[1]

Results.

The measurements were confined to mercury electrodes in approximately N./5 H_2SO_4 solutions, for which overpotential curves are given in the next part. The area of the electrode surface was taken as equal to the cross-sectional area of the containing tube. This implies that the effect of any creeping of the solution between the mercury and the walls of the glass vessel is negligible. This assumption, which has been made by others, appears to be justifiable, since measurements made in tubes of different diameters gave consistent results for the capacity per unit area of tube cross-section. Characteristic charging curves are given in Figs. 1 and 2.

From the slope of the curve (Fig. 1) showing the total charge as a

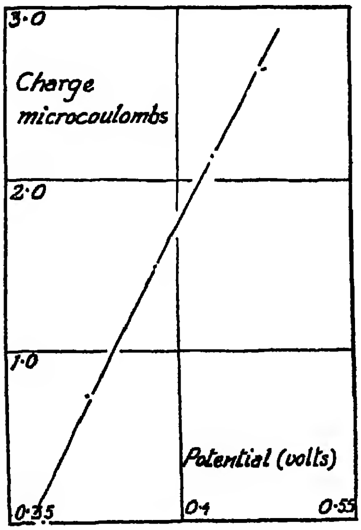

FIG. 1.

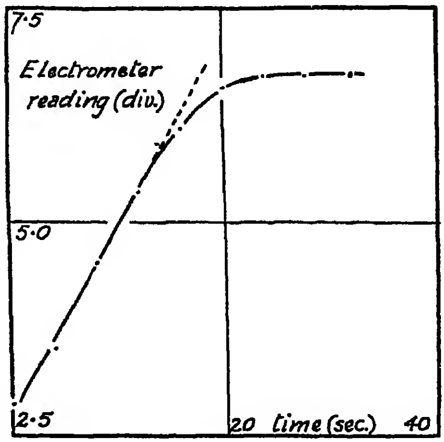

FIG. 2.

function of the potential, the capacity is found to be K=20·6 mfd./cm.². The calculation from the initial slope of the deflection-time curve (Fig. 2) is as follows:

$$\frac{d\theta}{dt} = 0{\cdot}225 \text{ cm./sec.}: \qquad \frac{dV'}{dt} = 0{\cdot}225/23{\cdot}3 = 0{\cdot}00966 \text{ v./sec.}$$

$$K = \frac{(i_2 - i_1)}{(dV/dt)} = \frac{0{\cdot}186}{0{\cdot}00966}/0{\cdot}95 \text{ mfd./cm.}^2 = 20{\cdot}3 \text{ mfd./cm.}^2.$$

The mean value obtained from 26 determinations made on mercury surfaces where the area varied from 7·7 sq. cm. to 0·95 sq. cm. was 20·2 ± 2 mfd./cm.².

This value of 20 mfd./cm.² is considerably higher than the value (6 mfd./cm.²) obtained earlier, when higher c.d. were used and the cathode was not protected by being completely enclosed in glass. In order to test whether the difference was due to the low rate of charging, the measurements were extended to a higher c.d. This was done by replacing the electrometer by an Einthoven galvanometer and camera. The procedure

[1] Bowden and Rideal, *Proc. Roy. Soc. A*, 1928, **120**, 59.

remained otherwise unaltered, except that it was necessary always to use the internal hydrogen electrode as reference electrode in order to reduce as far as possible the resistance in the galvanometer circuit. The calculation of the results was made by one or other of the methods indicated already for the measurements at small c.d. The measurements were made with a polarising current which varied from 0·02 to 0·006 microamp. The mean value obtained was 19 $\pm$ 2·4 mfd./cm.[2].

A Measurement of the Capacity of some Mercury/Non-aqueous Solution Interfaces.—In the previous paper overpotential measurements in some non-aqueous solutions are described. Preliminary results for hydrogen deposition from solutions of HCl gas in methyl alcohol, in pyridine, and from pure formic acid are given. The behaviour is in general similar to that in aqueous solution; that is, the overpotential appears to be proportional to log (c.d.), though the proportionality constant may differ from that in aqueous solution. A measurement of the capacity at the mercury/electrolyte interface may therefore be carried out just as for aqueous solutions.

Such measurements are of interest because of their relation to the structure of the double-layer. If the very simple Helmholtz picture of the layer is adopted, the capacity per unit area is given by

$$K = k/4\pi d$$

where k is the dielectric constant of the medium between the layers, and d is the distance. The value determined for a N./5 H_2SO_4 solution has been shown to be 20 mfd./cm.[2]. The ratio k/d is therefore about 22×10^7 e.s.u. The appropriate value to be taken for k is uncertain. If it is taken as unity, then the distance between the layers is $d = 0{\cdot}5$ A. This is a not unreasonable value. On the other hand, it is possible that the dielectric constant of the solvent must be taken into account, and some value between unity and that of the pure solvent be attributed to k. The reason for this is that the solvent molecules are not entirely excluded from the ionic layer in the solution, and these will affect the dielectric constant, increasing it to a value greater than unity. It may also be necessary to consider the variation in the distance d as the solvent changes, and also the dependence of the capacity on interfacial potential, though this is not very marked at high overpotentials. From this point of view, measurements of the capacity in solvents other than water are of interest.

The values found in the present work are tabulated below, together with the dielectric constant of the solvent.

TABLE I.—THE CAPACITY OF SOME MERCURY/ELECTROLYTE INTERFACES AND THE DIELECTRIC CONSTANT OF THE SOLVENT.

Solution.	Dielectric Constant of Solvent.	Capacity by Direct Measurement. mfd./cm.[2]
N./5 H_2SO_4 in water	81	20
Pure formic acid	58	67
HCl in methyl alcohol (N./10)	31	28
HCl in pyridine (N./25)	12	16

The measurements in the non-aqueous solutions are less reliable than those in H_2SO_4 aq. In alcohol, the capacity showed a tendency to decrease with time, and in the other cases, the potential range over which measurements could be made was restricted. But the results show clearly that there is no direct relation between the dielectric constant of the solvent and the capacity of the double-layer. The electrocapillary measurements of Frumkin [2, 3] support this conclusion.

[2] Frumkin, *Z. physik. Chem. A*, 1923, 103, 43 and 55.
[3] Frumkin, *Ergeb. exakt. Naturwiss.*, 1928, 7, 235, where a review of electrocapillarity results is given.

Discussion.

The value of 20 mfd./cm.² for the capacity at a mercury/sulphuric acid interface is considerably higher than the values previously obtained by the same method. It is in good agreement with the values obtained in the electrocapillary and expanding surface methods. Thus for a 0·1 N. solution of H_2SO_4 Gouy's [4] electrocapillary measurements lead to an average value of 21·0 mfd./cm.² between −0·5 and −0·7 v. (N. cal. scale), which was the range covered in the present measurements. The results obtained by Philpot [5] using the expanding surface method give a value of 21 mfd./cm.²; this is almost independent of the potential provided this is more negative than −0·6 v. Thus over the limited range of potential for which comparison is possible, the three methods now agree in giving values for the capacity of 20-21 mfd./cm.²; this in spite of the fact that in one case (the expanding surface measurement) the anion was different from that in the others.

The lower values of about 6 mfd./cm.² previously obtained [1, 6] are apparently due to some surface contamination. In this connection, a paper published while this work was in progress by Proskurnin and Frumkin [7] is of interest. It describes measurements of the capacity made by an alternating current method. A mercury electrode in, amongst others, a N. H_2SO_4 solution was polarised by a direct current; superimposed on this was a small alternating current, and the consequent potential variations were amplified and measured. The method is suitable for an investigation over an extended potential range and the results obtained were in agreement with Gouy's electrocapillary measurements. Any surface contamination of the mercury gave a low value for the capacity.

The results obtained in this work for the particular cases described support the conclusion that in general the three methods of determining the capacity lead to values in agreement. The results also show that there is no direct relation between the dielectric capacity of the liquid and the capacity of the double-layer.

Résumé.

La capacité d'une interface mercure-acide sulfurique, a été mesurée par la vitesse de charge de l'interface à de très faibles densités de courant. Le résultat obtenu (20 μF/cm.²), considérablement supérieur à celui trouvé précédemment par la même méthode, est en accord avec les valeurs déterminées par mesures d'électrocapillarité ou par une méthode de suspension de surface. Des mesures semblables dans l'alcool méthylique, la pyridine et l'acide formique, n'indiquent aucune relation directe entre la constante diélectrique du liquide et la capacité de la double couche à l'interface.

Zusammenfassung.

Die Kapazität an der Phasengrenzfläche zwischen Quecksilber und wässeriger Schwefelsäure wurde durch Messung der Geschwindigkeit der Aufladung der Grenzfläche bei sehr kleinen Stromdichten bestimmt. Der so erhaltene Wert (20 Mikrofarad/cm.²) ist weitaus höher als frühere Messungen nach derselben Methode ergeben hatten, aber stimmt gut mit den Werten überein, die mit Hilfe der Elektrocapillaritätsmethode und der Methode von Philpot bestimmt wurden. Ähnliche Messungen für Methylalkohol, Pyridin und Ameisensäure weisen nicht auf eine direkte Relation zwischen der Kapazität der Doppelschicht und der Dielektrizitätskonstante hin.

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[4] Gouy, *Ann. chim. physique*, 1903, **29**, 230.
[5] Philpot, *Phil. Mag.*, 1932, **13**, 775.
[6] Erdey-Gruz and Kromrey, *Z. physik. Chem. A*, 1931, **157**, 213.
[7] Proskurnin and Frumkin, *Trans. Faraday Soc.*, 1935, **31**, 112.

STUDIES IN ELECTROLYTIC POLARISATION:

II.—THE EFFECT OF THE SOLVENT ON THE HYDROGEN OVERPOTENTIAL. (i.)

By J. O'M. Bockris.

Received 13*th January*, 1947.

The balance of evidence relating to the two principal groups of theories of hydrogen activation overpotential [1] has not been markedly altered in the last decade because few critical tests of either group have been carried out. A factor which would seem to make possible clear experimental distinction between the two theories is that of the solvent effect. Thus, the changing solvent would alter a number of the factors which affect the overpotential, the more important of which are the solvation of the hydrogen ion, adsorption on the cathode, and the interfacial tensions gas-solution and cathode material-solution. The energy of solvation has received particular attention in the slow discharge theories of hydrogen overpotential,[2] and importance attaches to the factor of adsorption in most theories. Considerations directly connected with interfacial tension have received less attention in recent theoretical work, but they remain cogent in connection with possible secondary effects.[5]

Early work on the solvent effect on hydrogen overpotential was carried out by measurements of minimum overpotentials. Carrara [6] found a small decrease in overpotential in alcoholic solutions, but the sharpness of the inflexion point is even less in non-aqueous than aqueous solutions, and this considerably detracts from the value of the result. Thiel and Breuning [8] found that addition of bathotonic substances such as butyric acid or amyl alcohol to an aqueous solution increased the overpotential on a platinum cathode but according to Glasstone,[9] high concentrations of *iso*butyl alcohol, *iso*amyl alcohol or acetic acid cause the overpotential to decrease. The work of these authors was mainly concerned with attempts to correlate overpotential with interfacial tension; it has little cogency to modern concepts because the minimum overpotential is now regarded as having an uncertain meaning.[10]

Measurements of overpotential in non-aqueous solutions were first carried out by Swann and Edelmann,[11] who examined various cathodes in acetic acid solutions of sulphuric acid for c.d.'s between $5 \cdot 10^{-3}$ and $5 \cdot 10^{-2}$ amp. per sq. cm., the potentials being measured at an indefinite time after commencement of polarisation at a given c.d. These workers report results to which the Tafel equation [12] is not applicable. The overpotential is much higher than in aqueous solutions, and the relative order of the overpotential at a given c.d. is different from that in aqueous solutions. It seems probable that a large resistance error severely limits the value of these results.

[1] Hickling and Salt, *Trans. Faraday Soc.*, 1942, 38, 474; Wirtz, *Z. Elektrochem.*, 1938, 44, 303.
[2] Gurney, *Proc. Roy. Soc. A.*, 1931, 134, 137.
[3] *Trans. Faraday Soc.*, 1942, 38, 474.
[4] Eyring, Laidler and Glasstone, *J. Chem. Physics*, 1939, 7, 1053.
[5] *Trans. Faraday Soc.*, 1941, 37, 224.
[6] *Z. physik. Chem.*, 1909, 69, 75.
[7] *Ibid.*, 1901, 38, 601.
[8] *Z. anorg. Chem.*, 1913, 83, 329.
[9] *Trans. Faraday Soc.*, 1925, 21, 36.
[10] Baars, *Sitzungsber. Ges. Beförd. Naturwiss.*, Marburg, 1928, 63, 213.
[11] *Trans. Amer. Electrochem. Soc.*, 1930, 158, 179.
[12] Tafel, *Z. physik. Chem.*, 1905, 50, 641.

Lewina and Silberfarb [13] measured the hydrogen overpotential in ethyl alcoholic solution of HCl at a Hg cathode over a c.d. range of 10^{-6} — 10^{-2} amp. per sq. cm. The overpotential was found to be lower than in aqueous solution over the whole c.d. range being as much as 0·25 v. lower at a c.d. of 10^{-2} amp. per sq. cm. At higher c.d.'s the overpotential tended to reach a limiting value, unaffected by c.d. Novoselski [14] repeated Lewina and Silberfarb's work on a Hg cathode and found similarly, for this and the analogous system in methyl alcohol, that there is a lowering in comparison with aqueous solution.

Pleskov [15] examined the hydrogen overpotential in solutions of NH_4Cl in liquid NH_3 at − 50° c. on Hg, Pb and Ni electrodes by the direct method. On all metals there is an increase of overpotential in comparison with aqueous solutions. Assuming that the order of the temperature coefficient is the same as that in aqueous solution (about 2×10^{-3} v./°c.), and making allowance for this, the results show a general increase on a Ni cathode of about 0·1 v. Results on other cathodes are difficult to interpret owing to the reported presence of a visible film formed during electrolysis.

Hickling and Salt [5] measured the hydrogen overpotentials on Hg, Ww, platinised Pt, Pb, and Sn in solution of ethylene glycol with some subsidiary measurements for the first three metals in the corresponding cyclohexanol and ethyl alcohol solutions. An increase of overpotential is reported in all cases, and this amounts to 0·32 v. on Ww in cyclohexanol at 10^{-3} amp. per sq. cm. The *b* values of the Tafel equation are generally increased, but the form of the overpotential-log (c.d.) relation over the c.d. range used (10^{-3} — 1 amp. per sq. cm.) remain essentially unaltered.

Thus, little comprehensive work has been carried out on the solvent effect on overpotential, and the results of different authors often disagree. The available evidence seems to favour a lowering of overpotential in alcoholic solutions of HCl, but is insufficient to enable any general conclusions to be drawn. Non-alcoholic solvents have not been examined at known c.d. and ordinary temperatures ; there is no evidence of a possible relation between the properties of the solvent and its effect upon overpotential, and whether or not the influence of the solvent is characteristic of the electrode material, cannot be decided. Furthermore, attempted work in anhydrous solutions of alcohols is open to the objection that a very slight hydrolysis may produce a small quantity of hydroxonium ions which may be the entities discharged. It appears, therefore, that a series of determinations in aqueous/non-aqueous mixtures of varying composition might yield results of use, for it would then be possible to investigate the effect of changing amounts of hydroxonium ion. Studies on this and the other factors mentioned above have been carried out as far as the limitations of the choice of solvent, outlined in the next section, allow.

Experimental.

Choice of Solvent.—A suitable non-aqueous solvent for overpotential determinations must obey the following criteria as far as possible (cf. also Hickling and Salt [5]).

(i) It must be easily available and stable to light.

(ii) It must be a good ionising solvent, so that resistance errors in the use of the direct method can be reduced to a minimum.

(iii) It must be stable to N HCl for at least 12 hr.

(iv) It must be easily dehydrated, preferably without the addition of drying agents containing metallic ions.

(v) It must be stable to nascent hydrogen.

[13] *Acta physiochim.*, 1936, 4, 275.
[14] *J. Physic. Chem.* (*Russ.*), 1938, 11, 369.
[15] *Acta Physiochim.*, 1939, 11, 305.

It would be further advantageous if the solvent were water-miscible because then mixtures with water could be utilised.

The lower alcohols are the only solvents which completely satisfy these conditions. It is desirable, however, to use solvents of a non-hydroxylic character, e.g., formic and acetic acids. The ethers also are appropriate solvents, except for their low ionising properties. It was decided, therefore, to use as solvents, methyl and ethyl alcohol and ethylene glycol, formic and acetic acids, and diethyl ether and dioxane. Measurements were carried out in the pure anhydrous solution where practical and in most cases also in aqueous/non-aqueous mixtures of varying composition, for which systems measurements appear to be lacking. In systems containing acetic acid and dioxane, it was not practical to carry out experiments in anhydrous solutions owing to the high resistance of these and the consequent large ohmic overpotential introduced.

Purifications of Solvents and Preparation of Solutions.—Solvents for use in anhydrous systems and for systems in which measurements were carried out at c.ds. of less than 10^{-3} amp. per sq. cm. were subjected to a preliminary purification and dehydration, and the solvent was finally distilled in an atmosphere of dry H_2, which had been passed through three bottles containing alkaline pyrogallol, and collected in a vessel into which HCl could be passed ("solution vessel"). For aqueous-organic solvent systems, the organic solvent was purified and the appropriate amount of water added in air. The mixture was then boiled for 5 min. under reflux conditions in an all glass apparatus, allowed to cool during passage of H_2 and transferred to the solution vessel; HCl gas, appropriately dried, was then bubbled into the solvent, dry H_2 being passed at the same time to act as a stirrer. Small portions of the solution were removed from the solution vessel at intervals and analysed until appropriate conditions for the production of an approximately N solution ($1 \pm 0{\cdot}05$ N) had been determined. No further measures were taken to reduce the O_2 content of the solution for systems in which measurements were not made at c.ds. of less than 10^{-3} amp. per sq. cm. (cf. Hickling and Salt [16]).

For ethereal and aqueous acetic acid solutions in which some measurements were made at low c.d.'s, the general method of preparation of solution was similar to that described, but a vigorous deoxygenation was carried out by prolonged passage (24 hr.) of highly purified H_2 into the solution vessel before passing HCl. The H_2 was carefully purified by passage of cylinder H_2 through a series of alkaline pyrogallol bubblers containing sintered glass diffusion discs, and then through a glass tube maintained at 600° c., containing alternate layers of copper wire and palladinised asbestos (cf. Bowden and Rideal [17]).

Methyl alcohol was purified by addition of appropriate quantities of I_2 and Mg according to the method of Lund and Bjerrum. For ethyl alcohol, "Burnett" dehydrated alcohol was refluxed over CaO for 6 hr., distilled twice, the second time in an atmosphere of H_2. Commercially "pure" ethylene glycol was distilled and the middle fraction collected. This was again distilled and the fraction boiling at 197-198° was used as solvent material. 10 % aqueous formic acid was dehydrated by standing over $CuSO_4$ (anhydrous), the fraction boiling at 50° c. (110 mm.) being collected (m.p. = 8·4° c.).[18] A.R. acetic acid was dehydrated with the calculated quantity of P_2O_5, estimated cryoscopically. After several distillations, the fraction boiling at 116-119° was collected (m.p. = 16·5°). The ethyl ether used was Hopkin and Williams special Na-dried ether, further dried over Na for 24 hr. and distilled in a H_2 atmosphere. Technical dioxane was dried with KOH and BaO, distilled from the latter and then from Na, the fraction boiling at 101-102° (uncor.) being collected. It was redistilled from Na as required (m.p. = 11·75°).

[16] Hickling and Salt, *Trans. Faraday Soc.*, 1941, **37**, 319.
[17] Bowden and Rideal, *Proc. Roy. Soc. A.*, 1928, **120**, 59.
[18] Garner, Saxton and Parker, *Amer. Chem. J.*, 1911, **46**, 238.

Apparatus.—The electrolytic cell, described previously,[19] was connected to the solution vessel by a ground glass joint. The acid solution in the generating vessel was transferred by gas pressure into the electrolytic cell, which had been previously filled with H_2, the electrode having been placed in the cell immediately before this. At no point was the solution in contact with the tinfoil covering of the rubber bungs.

Reference Electrodes.—The hydrogen electrode was used to measure the cathode potential. Two electrodes of different areas were used and the potential of the working electrode was compared with each at every reading. The hydrogen electrodes were assumed to function reversibly in all the systems used (cf. [22] for acid methyl and ethyl alcoholic solutions and Hickling and Salt [5] for glycollic solutions). No direct verification of the reversibility of the hydrogen electrode in the other systems used here have been recorded, but measurements against the two electrodes of different surface areas indicate the same potential, unaffected by alterations of the bubbling rate, suggests that poisoning effects were absent.

Cathodes.—Pb, Cu and Ni cathodes were chosen as exemplifying respectively high, medium and low hydrogen overpotential metals. The Pb cathode (Goodlass-Wall, 99·993% Pb) was of cylindrical shape, and suspended by a Cu wire fused into it. Its diameter above the section immersed in solution was reduced to about 3 mm. to minimise variation of surface area caused by splashing. A rod of Hilger spectroscopically-pure Cu was used for the Cu cathodes. It was suspended in a glass tube with a Cu wire soldered to its upper end. Ni cathodes were in wire form and sealed into glass tubes, and connected to the outer circuit via a pool of Hg.

Pretreatment of the cathodes was similar to that used by Hickling and Salt.[20] For Pb and Ni cathodes, scraping with a sharp knife (cf. Grant [21]), interrupted by washing and rubbing with a filter paper for a standard time, was found to give the most reproducible results; for Cu, the scraping process was omitted. Cathodes treated with a knife were examined under the microscope for residual particles from the scraping process: none was observed. No given cathode was used for more than one electrolysis.

General Procedure.

The cathode potential was followed from the time of contact with the solution, until it had reached a steady state, which it generally attained in some 1-2 hr. Polarisation was then commenced, and procedure during measurements of the variation of overpotential at c.ds. of 10^{-3}, 10^{-2}, 5×10^{-2} and 10^{-1} amp. per sq. cm., was as described in Paper I. The effect of varying the rate of bubbling in the cathode compartments and the long time-decay of the cathode potential were noted at each c.d. in the various systems.

The ohmic overpotential tends, of course, to be greater in non-aqueous than in aqueous solutions, and careful tests were made to verify its reduction to a negligible value (see also ref. 19). In some solutions of increasing resistance, such as the aqueous-methyl and ethyl alcoholic systems the overpotential decreases considerably as the resistance of the solution increases. An exception is the measurements on a Cu cathode in ethereal solution. Here ohmic overpotential was very large at c.d.'s of about 10^{-3} amp. per sq. cm., and experiments were therefore made in the region of 10^{-6} amp. per sq. cm. The ohmic overpotential was still not negligible, and an attempt was made to allow for this by calculation from the equation

[19] Bockris (in press).
[20] *Trans. Faraday Soc.*, 1940, **36**, 1224.
[21] Grant, *ibid.*, 1928, **24**, 226.
[22] Tomicek and Feldmann, *Coll. Czech. Chem. Comm.*, 1934, **6**, 408; Demarest and Rieman, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 15; Goodhue and Hixon, *J. Amer. Chem. Soc.*, 1935, **57**, 1688.

$\eta = a + b \log d_c + IR$ at several c.d.'s, η being the apparent overpotential before correction. Uncertainties in this method are the value of b, which was assumed to be that in aqueous solution on a Cu cathode, and the assumed linear dependance of η on the logarithm of the c.d. The meaning of the results obtained in the ethereal system is thus less clear than those obtained in other systems. Measurements were carried out at room temperatures ($\pm$ 5° c. over all expts.).

Reproducibility of Results.

Reproducibility was lowest in the aqueous/non-aqueous mixtures and greatest in aqueous solution. The least satisfactory system was that containing glycol and water in which the mean variation was $\pm$ 0·04 v. In general the reproducibility was about $\pm$ 0·02 v., and in aqueous solutions $\pm$ 0·01 v.

Results.

Overpotential as a Function of the Solvent.—In the system methyl alcohol-H_2O-HCl (Fig. 1), the addition of methyl alcohol first causes an

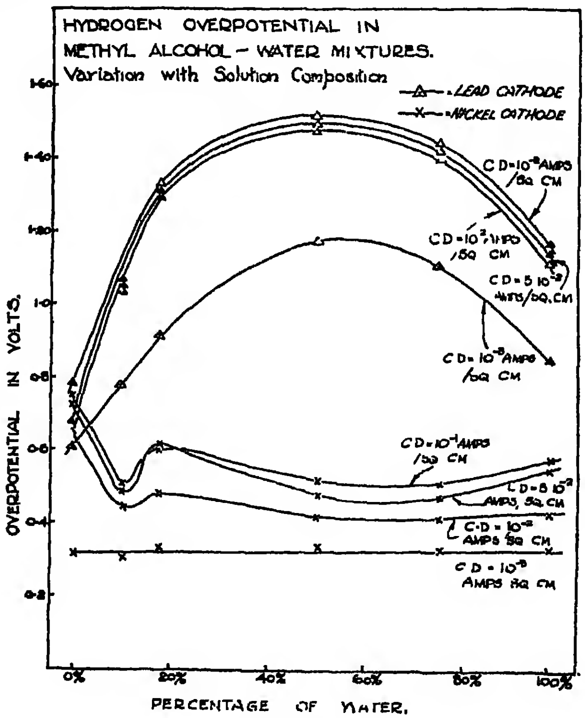

FIG. 1.

increase in the overpotential on a Pb cathode which passes through a maximum in the region of 45 % methyl alcohol. A fairly symmetrical decrease then occurs until for 100 % methyl alcohol the value of the overpotential is considerably less than that in aqueous solution. The same type of relation holds for the whole c.d. range examined. With Ni, when the c.d. is less than 10^{-3} amp. per sq. cm. the overpotential is little affected by the solvent composition. For c.d. greater than 10^{-3} amp. per sq. cm. there is a slow increase upon decrease of the water concentration

to an initial maximum at a composition of about 82 % methyl alcohol; the values then pass through a minimum and finally increase at 100 % methyl alcoholic HCl to values somewhat greater than those for aqueous solutions. The overpotential on Pb and Ni cathodes at higher c.d. in methyl alcoholic HCl tend to the same values, thus illustrating that the normal orders of the overpotential values may be displaced in non-aqueous solutions (cf. Swann and Edelmann [11]). The behaviour in the system ethyl alcohol-H_2O-HCl (Fig. 2) is analogous to that in methyl alcoholic solution except at the lowest c.ds. The value in 100 % ethyl alcoholic solution is considerably lower than that for aqueous solution, but the overpotential rises to a maximum at low ethyl alcohol contents, decreasing slightly to the value for pure aqueous solution. The lowering in 100 %

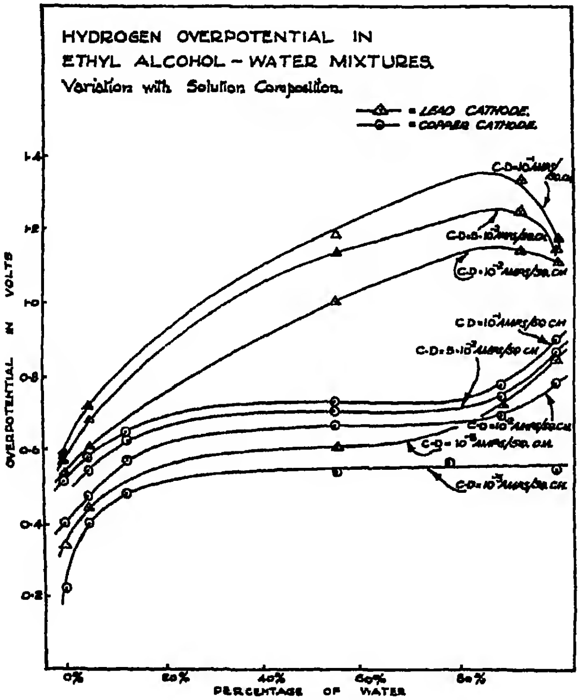

FIG. 2.

ethyl alcoholic solution is slightly less than that in pure methyl alcoholic solution. At a c.d. of 10^{-3} amp. per sq. cm. the behaviour at high ethyl alcohol contents resembles that for higher c.d., but now there is no maximum. For Cu, there is a lowering in pure ethyl alcohol similar to that for Pb. For aqueous ethylene glycollic solutions (Fig. 3), there is a uniform type of variation for the hydrogen overpotentials on Pb, Ni and Cu. Here the maxima found in the case of methyl and ethyl alcoholic solutions are replaced by minima. The Ni values are not greatly affected by the solvent composition. A slight difference only exists for the three metals between the values in ethylene glycollic and aqueous solutions.

In formic acid solution (Table I) the results observed for the less catalytically-active Pb and the more catalytically-active Ni again differ. The values for Ni are increased and those for Pb decreased; Cu behaves similarly to Pb. In the system acetic acid-H_2O-HCl (Fig. 4), on Cu and Pb there is a continuous lowering of the overpotential on increase of acetic

TABLE I.—OVERPOTENTIAL IN FORMIC ACID AND ETHEREAL SOLUTIONS OF HYDROGEN CHLORIDE.

Material.	Solvent.	Overpotential.				
		c.d. Amp./sq. cm.	10^{-3}	10^{-2}	$5 \cdot 10^{-2}$	10^{-1}
Pb	Water		0·85	1·10	1·14	1·15
	Formic acid		0·82	0·89	0·89	0·86
		$\Delta\eta$	− 0·03	− 0·21	− 0·25	− 0·29
Cu	Water		0·56	0·77	0·86	0·88
	Formic acid		0·52	0·61	0·65	0·67
		$\Delta\eta$	− 0·04	− 0·16	− 0·21	− 0·21
Ni	Water		0·33	0·42	0·53	0·56
	Formic acid		0·55	0·59	0·63	0·65
		$\Delta\eta$	+ 0·22	+ 0·17	+ 0·10	+ 0·09
		c.d. Amp./sq. cm.	10^{-6}	$5 \cdot 10^{-6}$	10^{-5}	
Cu	Water		0·04	0·10	0·15	
	Ether		0·02	0·07	0·12	
		$\Delta\eta$	− 0·02	− 0·03	− 0·03	

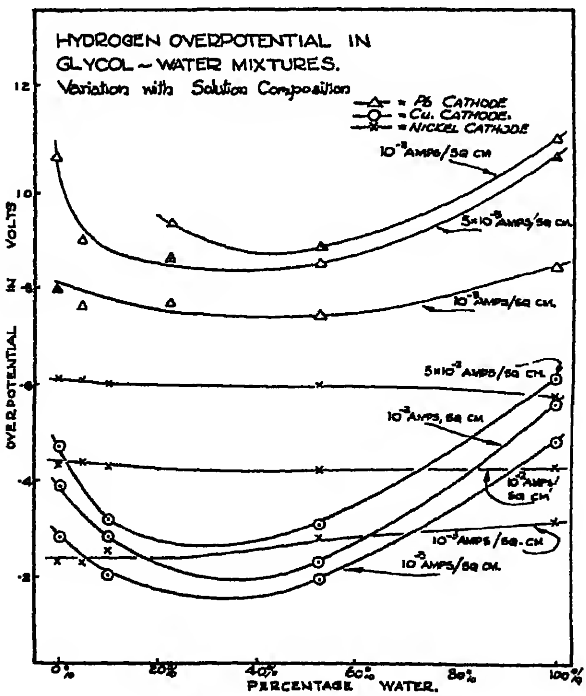

FIG 3.

acid content. For Ni there is a decrease in high acid contents giving place to an increase through a maximum at approximately 50 % acetic acid.

In the system dioxane-H_2O-HCl (Fig. 5) addition of dioxane brings about a decrease of the overpotential on Pb with decreasing slope towards the aqueous value. As in some other systems, a greater effect is observed at higher than lower c.d. For Ni a maximum is reached at a dioxane content of between 20 % and 40 %, according to the c.d., and then a rapid decrease towards the aqueous value. The overpotential-solvent relation at a c.d. of 10^{-3} amp. per sq. cm. passes through a minimum at a solution composition of about 50 % dioxane. In ethereal solution (see Table I), there is a decrease of overpotential of about 0·04 v. in comparison with

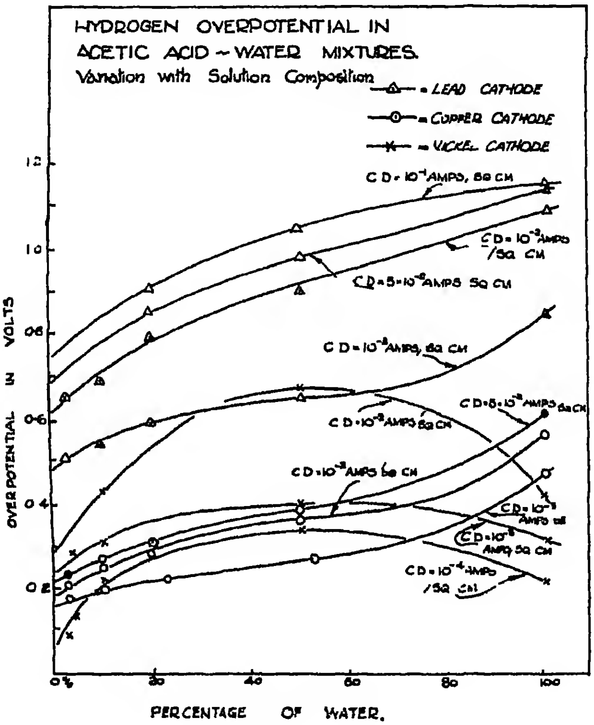

FIG. 4.

aqueous solution, in the c.d. range 10^{-6}-10^{-5} amp. per sq. cm., but this result rests upon the assumptions stated above.

Summarising therefore, it seems that for the catalytically-inactive metal Pb the hydrogen overpotential is generally less in the non-aqueous solutions, and that for the aqueous/non-aqueous mixtures it sometimes has a tendency to pass through well-defined maxima or minima at intermediate compositions. For the low overpotential metal, Ni, the solvent has less effect and the overpotential is either little changed or raised. The variations tend to be more complex. For the systems in which Cu has also been investigated, the general behaviour more closely resembles Pb than Ni; this can be correlated with the *b* value for Cu, which is high, similarly to that for Pb.

The Effect of the Solvent on the Overpotential-log Current Density Relation.—Plots of the overpotential log c.d. relation show that the Tafel equation applies essentially for all solvents at the lower c.ds.

The b values for the initial linear sections of the Tafel lines are functions of the solvent. Thus for lead there is a general decrease of slope in

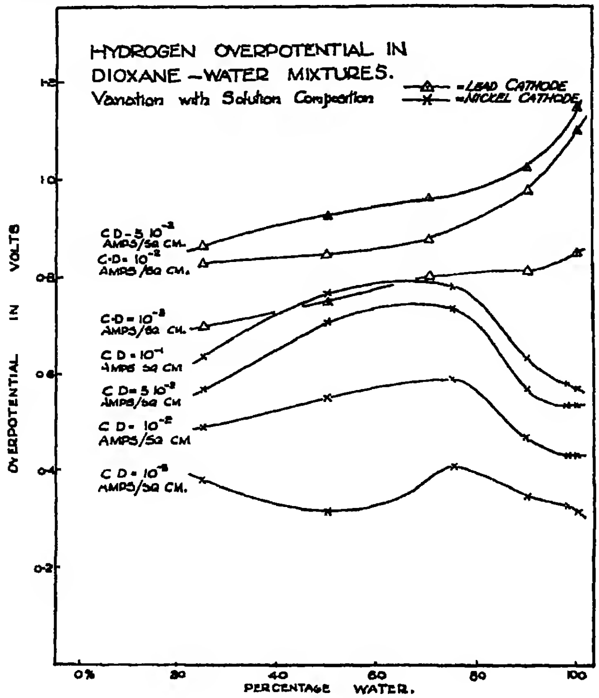

FIG. 5.

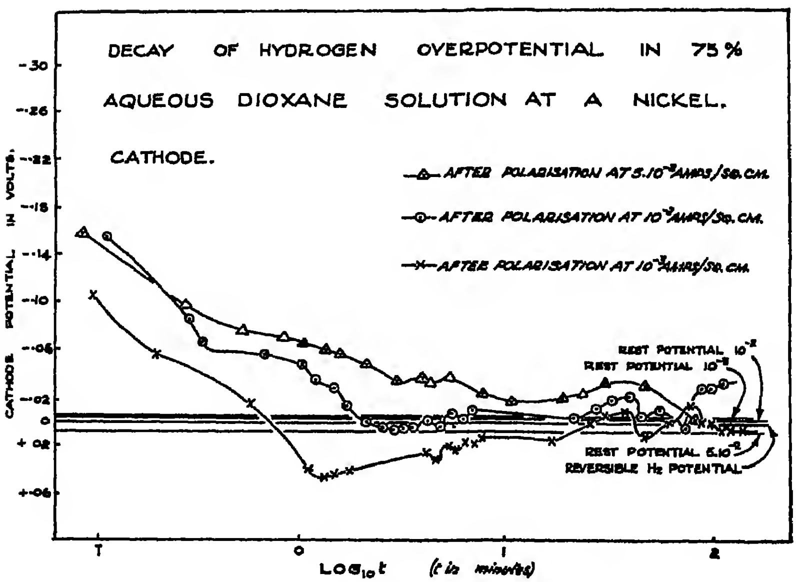

FIG. 6.

the presence of an organic solvent, except for some aqueous/non-aqueous mixtures with ethyl alcohol. For the less catalytically-active metal, Ni, however, the general trend is for the slope to increase. In general the changes are less than those for Pb. The variation of the b value for Cu follows the tendency for Pb. The shape of the Tafel lines is not greatly affected by the solvent, but there is a reduced tendency for the overpotential to reach a limiting value independent of c.d. in some systems in which the overpotential is lowered.

For a Pb cathode in anhydrous formic acid solutions, the overpotential is seen to decrease with increasing c.d. This is apparently anomalous (but cf. Hickling and Salt,[3, 20]).

The Effect of Stirring.—Stirring the electrolyte in the vicinity of the cathode by a stream of gas bubbles generally reduced the apparent overpotential at a c.d. greater than 10^{-3} amp. per sq. cm. The effect depended on the stirring rate until a critical rate after which no influence of bubbling rate was observed. Cathode material and solvent affected the influence of stirring but no regularities were obvious.

Long Time-Decay of Hydrogen Overpotential in non-aqueous/aqueous Mixtures.—Measurements were made of the decay of the hydrogen overpotential at long times (i.e. > few sec.) for systems containing methyl alcohol, ethylene glycol, acetic acid, and dioxane. There did not seem to be any systematic variation in the rate or manner of the long-time decay of the cathode potential with variation of the solvent (cf. Fig. 6).

Discussion.

It is possible to compare the present results directly only with those of Hickling and Salt,[5] because the work of Lewina and Silberfarb [13] and Novoselski [14] was carried out at comparatively low c.ds. The results of the present measurements for Pb and Ni in glycollic solutions agree essentially with Hickling and Salt's results for Hg, Pb and Sn, these authors finding the overpotentials to be little changed from those in aqueous solution. The results on Pb in ethyl alcoholic solutions, however, are not in accord with their conclusion that on the analogous metal Hg, there is no lowering of overpotential in alcoholic solvents. In so far as comparison is valid, the present results agree with those of Lewina and Silberfarb and of Novoselski, who found a lowering of overpotential in alcoholic systems.

The present work leads to the conclusion that the solvent effect on overpotential is a function of the cathode material as well as the solvent. It is consequently improbable that interfacial tension effects are involved as the metal-solution interfacial tension runs parallel to the gas-solution interfacial tension (cf. the Dupré equation), and is therefore constant for different metals in solutions of the same composition.

According to Gurney's [8] theory of irreversible electrode processes, the slow stage in overpotential is regarded as the neutralisation of solvated hydrogen ions by electrons from the cathode which reach the ion through the potential energy barrier at the cathode. The final integrated form of Gurney's equation for V_e, the "interphase potential," contains terms representing the work function of the metal, the solvation energy of the H^+ ion and the ionisation energy of the H atom. Presumably, therefore, in the corresponding expression for the overpotential, the two latter terms cancel out as they occur in the same form in the expression for the reversible potential. It appears, therefore, that according to Gurney's theory, the solvent should have no influence on the potential. It may be emphasised that this discrepancy with experimental evidence is not to be accounted for by some effect of the solvent on the work function or ionisation energy terms because it has been particularly stressed that "though directly observed work functions and contact potential differences are extremely

sensitive to surface impurities it is not these sensitive values which are relevant (here), but no matter what the surface contamination, always the values for the pure clean metal." [23] Further, the more detailed version of Gurney's theory, which takes into account the application of the Frank-Condon principle to the mechanism of neutralisation of the solvated ion and introduces a factor γ (where $\gamma > 1$) before all terms in the equation for the interphase potential, cannot form the basis of an interpretation of the solvent effect, for it concerns entirely the reaction

$$H^+ \text{ (solvent)} \xrightarrow{ne} H + n \text{ (solvent)},$$

and therefore should lead to an independence of a solvent effect on the cathode material.

These remarks apply in a more general way to other, non-quantum mechanical, neutralisation theories of overpotential, and even if it could be shown that the overpotential were connected to the desolvation energy of the hydrogen ion, the theory would still be in disagreement with experiment. Thus Goldschmidt [24] has determined the way in which the hydroxonium ion concentration varies with composition in an ethyl alcohol-water mixture containing HCl and his results show that the variation in no way corresponds with the variation of overpotential in this system.

According to the reaction rate theory of overpotential,[4] addition of methyl or ethyl alcohol, acetic acid, acetone, etc., to aqueous solutions breaks up the water structure in the vicinity of the cathode, and thereby lowers the energy of prototropic transfer of H^+ ions to the cathode, which is regarded as the rate-determining stage. A decrease of overpotential should therefore occur. This accords with some of the results obtained, but it is in marked disagreement with others: e.g. 20 % ethyl alcohol causes an increase on a lead cathode. In solutions in which hydrogen bonding between the hydrogen ion and solvent are absent it would be expected that a very considerable alteration in overpotential compared with that in aqueous solutions would ensue, yet in ethereal solutions on a copper cathode only a comparatively small lowering of overpotential is observed. The relation between the solvent effect and cathode material, also, does not seem to be in accord with the reaction rate theory.

The atomic hydrogen theory of overpotential, which has recently been interpreted in a new and powerful manner by Hickling and Salt,[3] would seem to offer, in a general way, a much more probable basis for the interpretation of the result, on the grounds of adsorption of the non-aqueous components from the solution by the cathode. It does not seem unreasonable to suggest that the adsorbed layer could act either as a positive or negative catalyst according to whether its space-consuming or catalytic properties predominated. It is hoped that this view can be developed after further experimental evidence has been obtained.

The author wishes to express sincere thanks to Dr. H. J. T. Ellingham for penetrating discussions of the work, and to Dr. A. Hickling for helpful comments on the paper.

Summary.

1. The hydrogen overpotential on Pb, Cu and Ni cathodes has been measured at c.d. mainly from 10^{-3} to 10^{-1} amp./sq. cm. in solutions of HCl in methyl and ethyl alcohols, ethylene glycol, formic and acetic acids, ether and dioxane and in mixtures of these with water except in the cases of formic acid and ether. The long time-decay and the effect of stirring have also been examined in these systems.

[23] Fowler, *Trans. Faraday Soc.*, 1932, **28**, 371.
[24] *Z. physik. Chem.*, 1914, **89**, 129.

2. On Pb the overpotential is generally lowered in non-aqueous solvents and passes through maxima and minima at intermediate compositions. On Ni there is generally a smaller solvent effect; the tendency is usually an increase on addition of the non-aqueous component. The solvent effect on Cu resembles that on Pb. The shape of the Tafel lines is affected by the solvent to a limited extent for all these metals.

3. The results do not seem to be in accord with known versions of the neutralisation or reaction rate theories. It is suggested that a catalytic mechanism, in which the adsorbed solvent molecules influence the rate of the reaction $H + H \rightarrow H_2$, may form a basis for the interpretation of the results.

Résumé.

(1) Le survoltage d'hydrogène sur des cathodes de Pb, Cu et Ni a été mesuré à des densités de courant, principalement de 10^{-3} à 10^{-1} amp./cm.^{2} dans des solutions de HCl dans les alcools méthylique et éthylique, le glycol, les acides formique et acétique, l'éther et le dioxane et dans leurs mélanges avec l'eau, excepté dans le cas de l'acide formique et des éthers. La décroissance du phénomène en fonction du temps et l'effet de l'agitation ont été aussi examinés.

(2) Sur Pb, le survoltage est généralement abaissé dans des solvants non aqueux et passe par des maxima ou des minima à des compositions intermédiaires. Sur Ni, le solvant a un effet plus faible, habituellement un accroissement du survoltage par addition de solvant non aqueux. L'effet du solvant sur Cu ressemble à celui sur Pb. Le solvant affecte la forme des lignes de Tafel pour tous ces métaux.

(3) Les résultats ne s'accordent pas avec les théories fondées sur la vitesse de réaction ou la neutralisation, mais avec un mécanisme catalytique, dans lequel les molécules adsorbées du solvant influencent la vitesse de la réaction : $H + H \rightarrow H_2$.

Zusammenfassung.

(1) Die Wasserstoffüberspannung an Pb, Cu und Ni—Kathoden in Lösungen von HCl in Methyl- und Äthylalkohol, Äthylenglykol, Ameisensäure, Essigsäure, Äther und Dioxan und (mit Ausnahme von Ameisensäure und Äther) Gemischen dieser Lösungsmittel mit Wasser wurde bei Stromdichten hauptsächlich zwischen 10^{-1} und 10^{-3} A/cm.^{2} gemessen.

(2) Die Überspannung an Blei in nichtwässerigen Solventien ist im allgemeinen niedriger als in Wasser und weist bei dazwischenliegenden Lösungsmittelzusammensetzungen Maxima und Minima auf. Cu verhält sich ähnlich. Bei Ni übt das Lösungsmittel in der Regel einen geringeren Einfluss aus. Gewöhnlich ruft die Beimischung des nichtwässerigen Bestandteils eine Erhöhung hervor. Der Verlauf der Tafel'schen Linien wird bei allen diesen Metallen bis zu einem gewissen Grad vom Lösungsmittel beeinflusst.

(3) Diese Resultate scheinen nicht mit den bekannten Versionen der Theorien der Neutralisation oder Reaktionsgeschwindigkeit im Einklang zu stehen. Es wird vorgeschlagen, dass ein katalytischer Mechanismus, in dem adsorbierte Solvensmoleküle die Geschwindigkeit der Reaktion $H + H \rightarrow H_2$ beeinflussen, möglicherweise eine Basis für die Erklärung der Resultate liefert.

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THE ELECTRODEPOSITION OF HYDROGEN ON PALLADIUM.

By H. P. Stout.

Received 15th October, 1946.

When hydrogen is liberated electrolytically at a palladium cathode a portion appears as hydrogen gas and the remainder is absorbed into the metal. The relation between current density and electrode potential for this system has been investigated by Knorr and Schwartz [1] who express their results in the form

$$\eta = -b \log \frac{AF + J}{AF},$$

where η is the overvoltage, J is the current density, and A a factor denoting the rate of absorption from the gas phase. This differs from the current density-potential relation for platinum electrodes only through the term AF, which would naturally be absent in the latter case as platinum does not absorb hydrogen to any extent. The reaction on palladium does not, however, appear to have been studied so exhaustively as that on platinum, and it was thought that, in view of the great absorptive powers of palladium for hydrogen, further experiments particularly with regard to the thermodynamic reversibility of the electrode might yield results of interest.

Experimental.

The cell and the electrical circuit used were the same as those described previously,[2] giving provision for the measurement of current and electrode potential. Aqueous solutions of sulphuric acid were used as electrolyte, made up from distilled water having a conductivity of about 10^{-6} mhos per cc. and Kahlbaum sulphuric acid previously distilled under reduced pressure. The solutions were saturated with hydrogen purified by passing through alkaline permanganate and alkaline pyrogallol, and then over heated palladinised copper. The gas was dried by passing over strong sulphuric acid and then through a liquid-air trap. The cathode of the cell was a piece of palladium foil welded to a palladium wire, which in turn was welded to a length of platinum wire, the latter being sealed into a soda glass tube. Before filling the cell the solution was boiled under reduced pressure with a stream of hydrogen pasing through, to remove carbon dioxide and oxygen. The cell was then exhausted by the water-pump and filled with hydrogen, after which the solution was blown in by hydrogen pressure.

Results.

(1) Cathodic Polarisation.—In N/5 sulphuric acid, with the electrode polarised cathodically, a linear relation between the electrode potential and the logarithm of the current density was obtained over a range from 10^{-5} to 10^{-3} amp. per sq. cm. At current densities below 10^{-5} amp. per sq. cm., however, the potential decreased less and less steeply as the current density decreased, typical curves being shown in Fig. 1. The slope of the linear portion of the curve, b, was found to vary with the previous treatment of the electrode, and while it might be as low as 75 mv. for a freshly cleaned electrode, rose to about 200 mv. with continued use.

[1] Knorr and Schwartz, *Z. Elektrochem.*, 1934, **40**, 38.
[2] Stout, *Trans. Faraday Soc.*, 1945, **41**, 64.

The curves were reproducible to about 5 mv. for a given electrode provided the slope was not greater than about 120 mv., but for greater slopes the reproducibility fell off considerably. The value of the factor $\alpha\left(=\dfrac{2{\cdot}3RT}{bF}\right)$ varied correspondingly between 0·8 and 0·5 over the range where reproducible results were obtained. Stirring the solution with hydrogen did

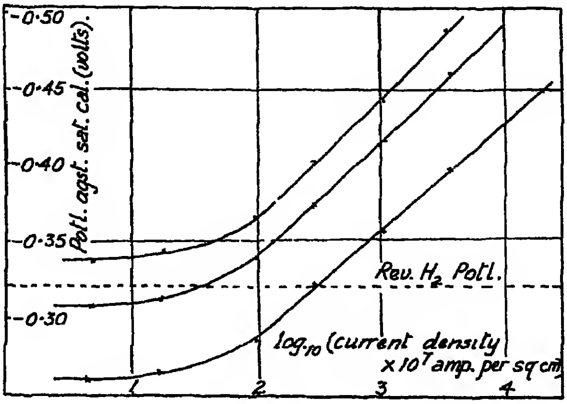

FIG. 1.

not affect the potential, the current being held constant, and thus it appears that this is a case of activation overpotential.[3]

It will be seen from Fig. 1 that the potential taken up by an unpolarised electrode is not in general equal to the reversible hydrogen potential, but may be either more or less negative. It was found that this potential was very dependent on the previous treatment of the electrode, being much more positive for a freshly cleaned electrode than for one subjected to prolonged cathodic polarisation, in agreement with results obtained by other workers.[4]

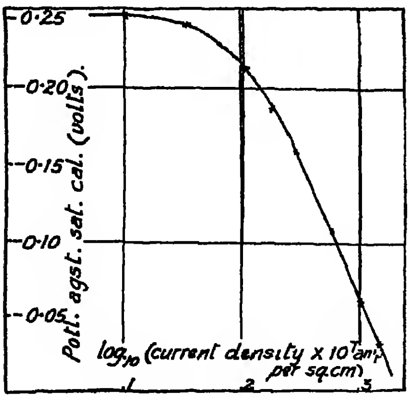

FIG. 2.

(2) Anodic Polarisation.—On making the electrode anodic, a similar relation was found between potential and logarithm of the current density, except that the slope was much greater than in the cathodic case. Fig. 2 shows a typical curve with $\alpha = 0{\cdot}3$, and it will be seen that as the current decreased the potential began to rise less steeply at about 10^{-5} amp. per sq. cm. and finally became constant at about 10^{-6} amp. per sq. cm. For current densities below 10^{-5} amp. per sq. cm. a linear relation between potential and current density was found, for both cathodic and anodic polarisation, and a typical curve is shown in Fig. 3, the slope being 1·3 v. per ma. A linear relation between potential and c.d. has been found for hydrogen deposition on platinum,[5] and is to be expected if the net current is

[3] Agar and Bowden, *Ann. Reports*, 1938, **35**, 90.
[4] Coehn and Specht, *Z. Physik*, 1930, **62**, 1.
[5] Volmer and Wick, *Z. physik. Chem. A*, 1935, **172**, 429.

regarded as the difference between the currents for deposition and solution of hydrogen ions. Taking these currents as

$$i_d = i_0 \, e^{\alpha_1 \eta F/RT}$$

and

$$i_s = i_0 \, e^{+\alpha_2 \eta F/RT}$$

the resultant is $i = i_d - i_s = -i_0 \dfrac{\eta F(\alpha_1 + \alpha_2)}{RT}$ for small η.

(3) Variation of Slope with Unpolarised Potential.—It was observed in some instances that during the cathodic polarisation the slope of the $V/\log i$ curve appeared to increase slightly as the unpolarised potential became more negative. The effect was small and difficult to distinguish from other changes in slope which are always liable to occur on prolonged polarisation, and its significance could be judged only by the application of statistical tests. A large number of $V/\log i$ curves were therefore obtained for several different electrodes polarised for varying times, so that the unpolarised potentials covered a range of about 100 mv., and the regression coefficient of slope on unpolarised potential calculated. The significance of the difference between this value and zero was then tested by the "t" test.[6] Table I gives the details of the calculation.

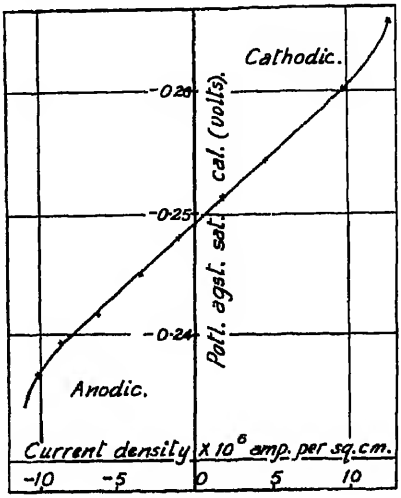

FIG. 3.

TABLE I

Mean potl. agst. cal. $\bar{V}$ mv.	300	No. of pairs of observations	49
Mean slope $\bar{b}$ mv.	109	No. of degrees of freedom	47
$\Sigma(V-\bar{V})^2$	$72{\cdot}1 \times 10^{-3}$	$n[\Sigma(V-\bar{V})^2]s^2$	$13{\cdot}9 \times 10^{-3}$
$\Sigma(b-\bar{b})^2$	$20{\cdot}2 \times 10^{-3}$	s^2	$4{\cdot}1 \times 10^{-6}$
$\Sigma(V-\bar{V})(b-\bar{b})$	$21{\cdot}3 \times 10^{-3}$	$t = r/s$	4·61
Regression coefficient $r = \dfrac{\Sigma(V-\bar{V})(b-\bar{b})}{\Sigma(V-\bar{V})^2}$	0·295	Value of t for $P = 1\%$	2·6

The regression coefficient is 0·295, which means that a change in the unpolarised potential of 1 mv. produces a corresponding change of about 0·3 mv. in the slope of the $V/\log i$ line. The standard deviation of the regression coefficient is 0·064 mv., giving a value for "t" of 4·61. The 1 % level for 47 degrees of freedom is 2·6 and the observed value thus shows clearly that the regression coefficient is significantly greater than zero.

[6] Fisher, *Statistical Methods for Research Workers*, 7th edn., p. 146.

(4) The Unpolarised Potential.—The experiments described give results very similar to those obtained for the electrodeposition and electrosolution of hydrogen at platinum electrodes,[7, 8] with the exception that whereas the unpolarised potential of a platinum electrode is generally within a few mv. of the reversible potential, the unpolarised potential of a palladium electrode may depart widely from this value. A freshly cleaned electrode may take up a potential as much as 60 mv. positive to the reversible potential, but on making cathodic for several hours at a current density of about 0·1 amp. per sq. cm. the unpolarised potential approaches the latter value and finally becomes more negative. On standing, however, the potential falls slowly to the reversible value where it remains constant, and by polarising the electrode anodically the potential can be made more positive until it eventually reaches the original value.

The difference between the potential of an unpolarised electrode and the reversible hydrogen potential was thought to be connected with the hydrogen content of the palladium, although the possibility that impurities deposited on the electrode might have some effect could not be overlooked. An experiment in which the effect of impurities was ruled out was then devised, consisting in the measurement of the potential of the inner surface of a palladium tube filled with sulphuric acid, when the

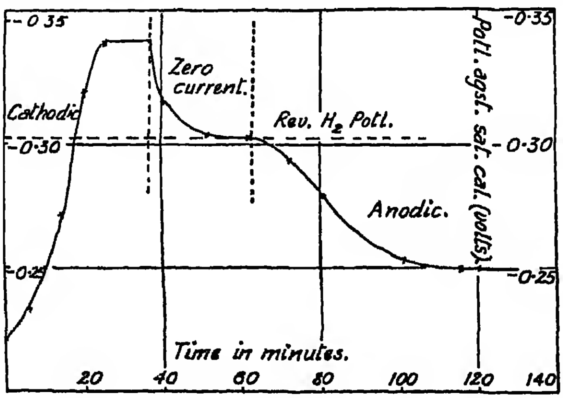

FIG. 4.

outer surface was polarised cathodically. The apparatus consisted of a palladium tube 6 cm. long, 0·15 cm. in diam. and having 0·01 cm. walls, each end being sealed into soda glass tubes with platinum sealing glass. The interior of the tube was filled with N./5 (approx.) acid and connected to a calomel cell, the outer surface being surrounded by a bath of N./5 acid and made cathodic in the latter at a current of 0·1 amp. The potential inside the tube was then measured at different times, a potential-time curve so obtained being shown in Fig. 4. The potential was initially about 80 mv. positive to the reversible hydrogen potential, and rose steadily to a constant value about 30 mv. more negative than the latter. On switching off the polarising current, the potential fell fairly rapidly to the reversible value, where it remained constant. On polarising the outer surface anodically the potential fell slowly to more positive values.

From these results it seems clear that hydrogen produced at the outer surface of the tube diffuses into the metal and thus affects the potential of the inner surface, and the quantitative relation between the quantity of hydrogen in the metal and the electrode potential now remains to be determined. The former quantity may conveniently be obtained from

[7] Bowden, *Proc. Roy. Soc. A*, 1929, **126**, 107.
[8] Volmer and Wick, *loc. cit.*

the relative change in resistance, while the latter is measured against calomel in the usual way.

Experiments were carried out with an electrode in the form of a loop of palladium wire, the resistance being measured by comparing the potentials developed across it and a standard resistance in series when current was passed through the pair. Platinum potential leads were welded to the wire in order to avoid any ohmic potential drop being included in the resistance. Before use the wire was heated electrically in a high vacuum to remove any hydrogen contained in it, the heating being continued until the resistance became constant. The wire was then polarised cathodically for a given time at a current density of 10^{-2} amp. per sq. cm., and the potential against calomel measured with the current off. The solution was then forced by hydrogen pressure from the cathode compartment to the anode compartment and the resistance of the electrode determined. The solution was then returned to the cathode compartment and polarisation continued for a further period. The resistance was then re-measured, and the whole process repeated until a constant value of the resistance was obtained. The quantity of hydrogen in the wire was estimated from data given by Kruger and Gehm[9] for the relative change in resistance with change in the ratio of atoms of hydrogen to atoms of palladium, assuming that the wire was originally free from hydrogen.

The relation between potential and hydrogen content of the wire is shown in Fig. 5, and is similar to that found by Coehn and Specht.[10] It will be observed that the reversible hydrogen potential is attained when the ratio of hydrogen atoms to palladium atoms, r, is 0·35, and that the most negative potential reached corresponds to r equal to 0·65. It was not found possible to exceed the latter value under the conditions of the experiment, and if Fig. 5 is compared with Fig. 4, it will be seen that the most negative potential attained by both wire and tube was the same, about 0·33 v., a value presumably characteristic of $r = 0·65$.

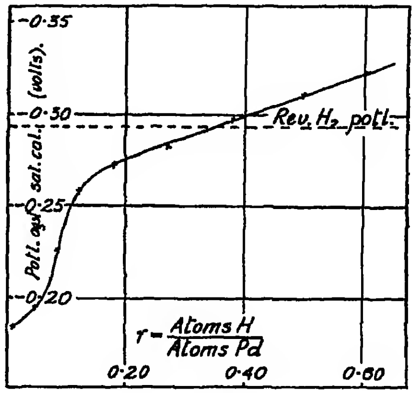

FIG. 5.

If the electrode is acting reversibly, and taking up a potential corresponding to equilibrium between hydrogen ions in solution and hydrogen in the metal, the relative activity of the latter may be calculated from the equation

$$E - E_0 = -\frac{RT}{F} \ln a_H,$$

where E is the potential at activity a_H, and E_0 is the most negative potential recorded. This equation defines the activity at the latter potential to be unity, a definition which is, of course, quite arbitrary. The activities calculated in this way are shown plotted against the ratio of hydrogen to palladium atoms in Fig. 6, from which it will be seen that for r between 0·10 and 0·55 the activity is directly proportional to the hydrogen content.

Discussion.

The experiments described show that the electrodeposition and electrosolution of hydrogen at palladium electrodes are reactions exhibiting

[9] Kruger and Gehm, *Ann. Physik*, 1933, 16, 174.
[10] Coehn and Specht, *loc. cit.*

activation overpotential, and that the kinetics are very similar to those for the corresponding reactions at platinum electrodes. A linear $V/\log i$ relation appears to hold for all states of activity of the electrode but there is no evidence to show that the absorption of hydrogen from the gas phase is important, as suggested by Knorr and Schwartz.[11] The potential taken up by an unpolarised electrode is dependent on the hydrogen content of the electrode, becoming more negative as the hydrogen content increases. At such an electrode, hydrogen in the metal will be in equilibrium with hydrogen ions in the solution, via hydrogen adsorbed on the electrode surface. An increase in hydrogen content of the metal would be expected to cause an increase in the surface concentration of hydrogen, thereby sending the potential more negative, just as at a true reversible hydrogen electrode an increase in gas pressure sends the potential more negative, presumably by increasing the surface concentration. In the case of the palladium electrode, hydrogen in the gas phase would not be expected to exert any influence on the surface concentration, as experiments on the absorption of hydrogen from the gas phase show that over the range of hydrogen content considered the quantity of hydrogen in the metal is not controlled by the gas pressure, although the latter has a definite value.[12]

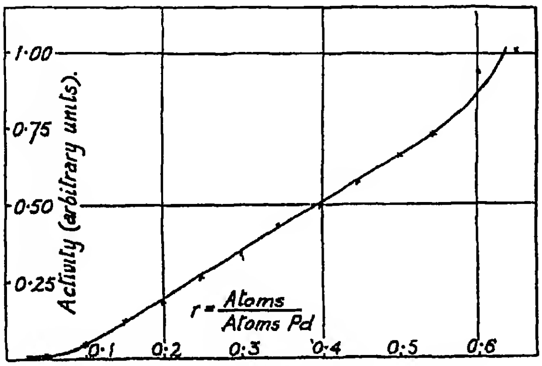

Fig. 6.

The hydrogen ions discharged at the electrode may be removed in two ways, by absorption in the metal, and by the formation of gaseous hydrogen. In the case of absorption it has been shown[13] that a rate-controlling process occurs at the metal-surface interface, except in the case of very active electrodes where the passage across the interface is rapid compared with diffusion in the metal. For electrodes activated by anodic polarisation and containing only a small concentration of hydrogen, it would be expected that the rate of absorption of hydrogen would have a maximum value determined by the rate of diffusion in the metal, and that as the current increases the rate of absorption would keep pace with it until the limiting rate is reached. At this point the alternative process, the formation of gaseous hydrogen, must commence if the current is increased further, and this process will follow the usual $V/\log i$ relation. As the concentration of hydrogen in the metal increases the rate of diffusion of hydrogen away from the metal-surface interface will decrease, and so the rate of absorption of hydrogen into the metal will decrease. Finally when $r = 0{\cdot}65$ the rate of absorption into the metal is zero, and all the hydrogen must disappear in gaseous form. The electrode is now functioning similarly to a platinum electrode, except that the surface concentration of adsorbed atoms will be much higher. When the current is cut off the electrode will tend to take up the reversible hydrogen potential, with consequent decrease in concentration of adsorbed atoms. This decrease will be counteracted by hydrogen diffusing out from the metal to the

[11] Knorr and Schwartz, *loc. cit.*
[12] Gillespie and Hall, *J. Amer. Chem. Soc.*, 1926, 48, 1207.
[13] Barrer, *Trans. Faraday Soc.*, 1940, 36, 1235.

surface, but eventually the potential will fall to the reversible value, where it will remain.

The fact that the slope of the $V/\log i$ line corresponding to the formation of gaseous hydrogen, increases as the potential of the unpolarised electrode becomes more negative suggests that the rate-determining process in this case lies in the recombination of adsorbed atoms to form molecules. For an increase in slope means a decrease in α and this is associated with an increase in concentration of adsorbed atoms, as evidenced by the change in potential. Now on the simple theory of the recombination of atoms, α should equal 2, but it has been shown [14] that this is only true for a sparsely covered surface, and that for a surface which is approaching saturation α may be much less than 2, particularly if there are strong repulsive forces between the adsorbed atoms. Under such conditions, α would be expected to decrease as the concentration of adsorbed atoms increases, finally becoming zero as the surface becomes completely covered.

Other rate-determining processes, such as ion neutralisation or the reaction between an adsorbed atom and an ion in solution, would be expected to be facilitated by an increase in the concentration of adsorbed atoms, with corresponding increase in α, instead of the decrease as actually observed. Thus it seems likely that here the rate-controlling process in the formation of hydrogen molecules is the desorption of atoms.

The condition of hydrogen dissolved in palladium is a matter of considerable interest, and the experiments described have some bearing on this point. The conduction electrons in palladium are in the s and d bands, and these overlap, the density of the d states, however, being much greater than that of the s states. It is considered that there are 0·55 to 0·6 s electron per atom, which out of a total of 10 leaves 9·45 to 9·40 electrons for the d band.[15] As the maximum number of electrons which can be accommodated in the d band is 10, there will remain 0·55 to 0·6 vacant states per atom in this band. These vacant states account for the high paramagnetic susceptibility of palladium and, on alloying with hydrogen, this susceptibility decreases and becomes zero when about 0·6 hydrogen atoms per palladium atom have been added,[16] presumably through the filling up of the d band with electrons supplied by the hydrogen, which will therefore be completely ionised. Any further increase in hydrogen content means either that electrons will start to fill up the s states, or that hydrogen atoms will dissolve un-ionised. In either case, as pointed out by Lacher,[17] this implies that one process of solution ceases at $r = 0{\cdot}6$ approximately. The fact that under the conditions described it proved impossible to increase r above 0·65 is thus in good agreement with these conclusions. So long as the hydrogen in the metal is ionised it might be relatively easy for an ion in solution to be transferred to the metal lattice, but if hydrogen atoms are required, the transfer from solution to metal might be much more difficult. It may be noted that values of r as great as 0·8 have been reported,[18] but the system appeared to have been rather unstable under these conditions.

The work described was carried out in the Laboratory of Physical Chemistry, Cambridge, and my thanks are due to Prof. Norrish for the facilities afforded me. I am also indebted to Dr. J. N. Agar and Dr. F. P. Bowden for many valuable discussions. Acknowledgement is due to the Chemical Society for grants for apparatus.

[14] Okamoto, Horiuti, and Hirota, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **29**, 223.

[15] Mott and Jones, *Properties of Metals and Alloys* (Oxford, 1936), p. 190.

[16] Svensson, *Ann. Physik.*, 1933, **18**, 299.

[17] Lacher, *Proc. Roy. Soc. A*, 1937, **161**, 525.

[18] Bennett, *J. Amer. Chem. Soc.*, 1939, **61**, 2683.

Summary.

The electrodeposition and electrosolution of hydrogen at palladium electrodes in aqueous solutions of sulphuric acid are irreversible processes giving linear $V/\log i$ curves. The potential taken up by an unpolarised electrode is not the reversible hydrogen potential, but a potential determined by an equilibrium between hydrogen ions in solution and hydrogen absorbed in the electrode, and is more negative the higher the concentration of the latter. The linear $V/\log i$ relation is considered to be due to a rate-determining process in the formation of gaseous hydrogen and for this, α decreases as the unpolarised potential becomes more negative. This is ascribed to an increase in concentration of adsorbed atoms, which under certain conditions will reduce the facility with which such atoms combine to form molecules.

The maximum quantity of hydrogen taken up by palladium electrolytically corresponds to a ratio of 0·65 atom of hydrogen to 1·0 atom of palladium, in agreement with the view that hydrogen dissolves ionised its electrons going to fill up the vacant *d* states of the palladium, which number about 0·6 per atom.

Résumé.

Le dépôt et la dissolution électrolytiques de l'hydrogène à l'électrode de palladium dans des solutions aqueuses d'acide sulfurique sont des processus irréversibles, dont les courbes $v = f(\log i)$ sont des droites. Une électrode non polarisée prend un potentiel qui n'est pas le potentiel réversible de l'hydrogène, mais qui est déterminé par un équilibre entre des ions hydrogène en solution et des ions absorbés par l'électrode, et il est d'autant plus négatif que la concentration de ces derniers est plus grande. On considère que la relation linéaire $v = f(\log i)$ est dûe à un processus qui détermine la vitesse, dans la formation d'hydrogène gazeux, et pour ce processus, α décroît lorsque le potentiel de l'électrode dépolarisée devient plus négatif. Ceci est attribué à un accroissement de la concentration des atomes adsorbés, qui, dans certains cas, diminuera la facilité avec laquelle de tels atomes se combinent pour former des molécules.

La quantité maximum d'hydrogène que le palladium peut prendre électrolytiquement, correspond à un rapport de 0·65 atome d'hydrogène pour 1·0 atome de palladium, en accord avec le point de vue selon lequel l'hydrogène se dissout ionisé, ses électrons allant remplir les positions vacantes du palladium, qui sont environ 0·6 par atome.

Zusammenfassung.

Die elektrolytische Abscheidung und elektrolytische Lösung von Wasserstoff an Palladiumelektroden in wässerigen Schwefelsäurelösungen sind irreversible Prozesse, die lineare V-$\log i$ Kurven ergeben. Die Spannung, die eine unpolarisierte Elektrode annimmt, wird von einem Gleichgewicht zwischen Wasserstoffionen in Lösung und an der Elektrode absorbiertem Wasserstoff bestimmt und wird umso mehr negativ je höher die Konzentration des letzteren ist. Die lineare Beziehung zwischen V und $\log i$ wird von einem geschwindigkeitsbestimmenden Prozess in der Bildung des gasförmigen Wasserstoffs hervorgerufen. Die Maximalmenge an Wasserstoff, die Palladium elektrolytisch aufnehmen kann, ist 0·65 Wasserstoffatome per Palladiumatom. Dies bestärkt die Anschauung, dass der Wasserstoff sich in ionisierter Form auflöst; die Wasserstoffelektronen füllen dann die leeren *d*-Zustände in Palladium auf, deren Anzahl ungefähr 0·6 pro Atom beträgt.

THE POLARISATION OF PLATINISED PLATINUM ELECTRODES IN DILUTE HYDROCHLORIC ACID.

By P. M. Bryant and G. E. Coates.

Received 28th January, 1947.

The polarisation, or departure from the reversible potential, observed during the discharge of hydrogen ions at an electrode is generally considered to be due to three effects hitherto regarded as quite separate, viz., (1) hydrogen overvoltage, (2) concentration polarisation, and (3) resistance overvoltage. The characteristic features of these were reviewed in 1938 by Bowden and Agar.[1] Resistance overvoltage is due to the potential arising from the product of the polarising current and the resistance between the working cathode and the reference electrode. Whereas this potential at one time prevented the measurement of polarisation in dilute solutions at high c.ds. (the resistance overvoltage could not be separated from the other polarisation terms), such measurements can now be made free from any resistance term by means of the recently developed technique of Hickling and Salt.[2, 3] The latter is an improvement of the commutator method using electronic devices both to interrupt the polarising current and to measure the minimum potential attained at the end of the period of interruption. Since no current flows during the period when the polarisation is measured, the results are free from the unwanted resistance term. By measuring the minimum potential for a wide range of periods of interruption (about 10^{-5} to 0·1 sec.) both the time-decay of the polarisation and the steady value may be obtained, the latter by extrapolation to zero time of interruption.

Polarisation measurements up to high c.d.'s in relatively concentrated acids (to avoid concentration polarisation), made possible by this technique, have led to a revised theory of hydrogen overvoltage.[4] The polarised cathode is regarded as an atomic hydrogen electrode, whose potential is given by

$$\pi = - 1{\cdot}98 - \frac{RT}{F} \log_e P,$$

where $-1{\cdot}98$ is the standard potential of atomic hydrogen and P the partial pressure (in atmos.) of atomic hydrogen at the electrode. The latter quantity is considered to be connected with the amount of hydrogen adsorbed on the electrode by means of the adsorption isotherms. This interpretation satisfactorily relates the overvoltage, and its variation with c.d., to the catalytic and adsorption properties of the metals studied.

The same experimental method has been used to measure concentration polarisation in relatively *dilute* acid solutions.[5] Concentration polarisation has always been considered as an effect arising *in the electrolyte*, being the deviation of the electrode potential from its reversible value caused by local concentration changes in the immediate vicinity of the electrode. This is in contrast to true overvoltage which arises *at the electrode*. Consequently it has been assumed [1, 6] that concentration polarisation is independent of the nature of the electrode, but depends on electrolyte composition, c.d. and temperature. The principle of the method was to measure the total polarisation, free from resistance overvoltage, against

[1] Bowden and Agar, *Ann. Reports*, 1938, 90.
[2] Hickling, *Trans. Faraday Soc.*, 1937, 33, 1540.
[3] Hickling and Salt, *ibid.*, 1941, 37, 450.
[4] Hickling and Salt, *ibid.*, 1942, 38, 474.
[5] Coates, *J. Chem. Soc.*, 1945, 484.

a reversible hydrogen electrode in the same solution, and to subtract the known hydrogen overvoltage for the given electrode material and c.d. (hydrogen overvoltage does not appear to vary appreciably with p_H [1, 4]). Closely similar concentration polarisations were obtained in this way using platinised platinum and tungsten electrodes in 0·1 N. HCl at 20° over a c.d. range from 0 to 1 amp. per sq. cm. Platinised platinum electrodes are particularly suitable for these measurements since the overvoltage term is low and decays very slowly with time.[3] With such electrodes the effect of acid concentration from 0·05 to 0·2 N., temperature, and the addition of neutral salts and weak acids, have been studied.[5]

Polarisations observed in dilute acids containing excess neutral salt (e.g. 0·2 N. HCl + 2 N. KCl) are relatively easy to interpret. The potential increases slowly with c.d. up to a critical region where it rises very sharply, and finally, in the region of 0·8 to 1 v., it remains almost constant. At c.d.'s above the maximum rate at which hydrogen ions can reach the electrode by diffusion, the p_H of the solution in the immediate vicinity of the electrode rises sharply to the alkaline region where water has a high buffer capacity and hence the potential, after rising sharply, no longer changes rapidly with c.d.

Polarisations in dilute acids containing no added electrolyte, hydrogen ions being the only cations present, provide a more difficult problem. At c.d.s of the order of 1 to 2 amp. per sq. cm., polarisations of 0·7 to 0·9 v. have been observed in 0·05 N. HCl at 20° C. This degree of polarisation could not be due to a simple concentration difference since it would correspond, by the expression for the potential of a concentration cell with liquid junction, to an impossible electrode p_H of about 40. Further, in the absence of any cations but hydrogen ions the electrode p_H could not rise above 7 unless there were more negative than positive ions near the electrode. This polarisation was tentatively explained on the assumption that a slight degree of electrical unbalance was, in fact, brought about by sufficiently rapid electrolysis; this would result in a considerable potential between the unbalanced layer of electrolyte near the electrode and the body of the solution, the layer being negative and hence facilitating the movement of hydrogen ions towards the cathode to the extent required by the c.d. imposed. It was suggested that the p_H at the electrode did not rise above the weakly acid region, and that the greater part of the observed polarisation at high c.ds. was due to a diffuse double-layer potential set up by this slight electrical unbalance in the immediate vicinity of the electrode.

The purpose of the experimental work described below was to extend concentration polarisation measurements to more dilute solutions of pure acids, with particular attention to the decay of the polarisation with time, an aspect not emphasised in the previous work.

Experimental.

The apparatus and method were similar in principle to those described previously.[5] The reference (reversible) hydrogen electrode was about 3 sq. cm. in area and was platinised by a standard method.[6] The working electrodes A and B were short lengths of platinum wire $0{\cdot}044_8$ cm. diam. sealed into soda glass, and areas $0{\cdot}098_9$ and $0{\cdot}102_8$ sq. cm. respectively. The activity and freedom from poisoning of these electrodes were tested by measurement of hydrogen overvoltage in N. HCl and by checking their potentials against a AgCl electrode (with precautions against the deposition of silver on the platinum).

The electrolyte was prepared from constant-boiling mixture HCl; it was freed from air by bubbling purified hydrogen through it, and was then kept under a hydrogen atmosphere in a reservoir attached to the

[6] Popoff, Kunz and Snow, *J. Physic. Chem.*, 1928, 32, 1056.

electrolysis apparatus. The platinum wire anode was separated from the remainder of the electrolytic cell by a sintered glass plate, and during electrolysis the anode products were removed by maintaining a steady flow of electrolyte through the cell and out of the anode compartment. The all-glass cell was surrounded by a jacket through which water from a thermostat was circulated. During measurements with the more dilute solutions at high c.ds. care was taken, by a more rapid flow of electrolyte and passage of current for short periods only, to avoid depletion of HCl in the cell.

The electrical apparatus was similar to that previously described, with the exception that the interruption pulses were squared by application to the grid of a Mazda SP 41 valve. By this means square pulses of quite definite length were obtained (the pulses being delivered to the cell in the form of square interruptions of the otherwise steady polarising current). The electrical circuit has since been further improved and will be described *in greater detail in a subsequent communication.*

Concentration of Hydrochloric Acid.—Polarisations at c.ds. up to 0·8 amp. per sq. cm. at 25°, measured over the concentration range 0·01 to 0·05 N., are shown in Fig. 1. These curves were obtained by plotting the observed polarisations against time of interruption of the polarising current and extrapolating to zero time. The small hydrogen overvoltage, as measured in N. HCl, was subtracted from the total polarisation, leaving what we regarded as the concentration polarisation. Two points of interest arise from these curves, first, the existence of maxima and second, the increase of maximum polarisations with acid concentration. Both the polarisation and the c.d. at the maxima increase linearly with the acid concentration. The decrease of potential at high c.ds. may be due to the increased stirring by gas evolution and to local heating at and near the electrode; both these effects might be expected to decrease polarisation.

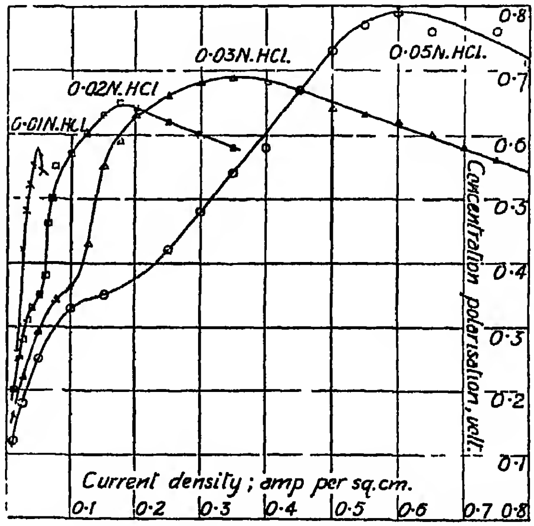

FIG. 1.—Effect of acid concentration on polarisation.

Decay of Polarisation.—At all concentrations and c.ds. investigated the polarisation fell to a low value, of the order of 0·1 v. or less, by a tenth of a second after interrupting the polarising current. Some of the time decay curves measured with 0·02 N. HCl at 25° are shown in Fig. 2; these were selected as representative from a large number of experiments. The most remarkable feature of these curves is the transition, in the narrow c.d. range 0·05 to 0·075 amp. per sq. cm., between two wholly different types of time-decay. This behaviour was observed quite generally; some new process appears to take place at all c.ds. above a critical range, characterised by the maintenance of constant potential until nearly $\frac{1}{100}$ sec. after the polarising current is switched off. Between $\frac{1}{100}$ and $\frac{1}{10}$ sec. the potential falls very rapidly, the curves for different c.ds. lying very close together. The transition between the two types of decay

curve corresponds to an inflexion in the polarisation—c.d. curve, which generally occurs at a potential in the region of 0·3 to 0·5 v. As the acid concentration is increased, the transition is observed at higher c.ds.

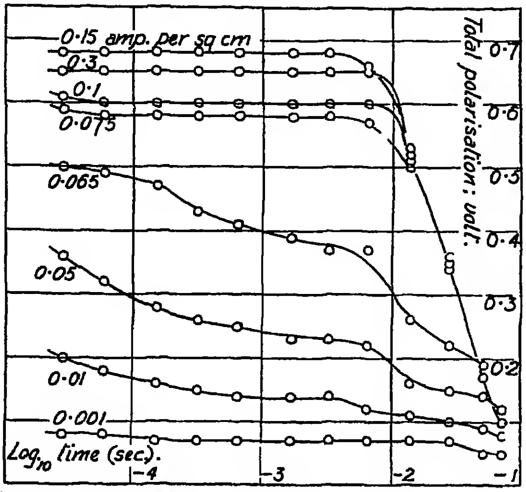

FIG. 2.—Time-decay of total polarisation; 0·02 N. HCl, 25°, electrode A.

Ageing of the Electrode.—Only one of the two electrodes originally prepared was used for all the experiments so far described, while the other was kept in distilled water for comparison purposes should any suspicion of poisoning arise. However, the apparatus was designed carefully to avoid any risk of poisoning, and there is no evidence that the electrode at any time became poisoned. Furthermore, the time-decay curves obtained with this electrode (A) differ in a radical and striking manner from the very rapid polarisation decay characteristic of poisoned platinised platinum electrodes.[3] Poisoned electrodes also become highly polarised even at low c.ds. of the order of 10^{-3} to 10^{-2} amp. per sq. cm.

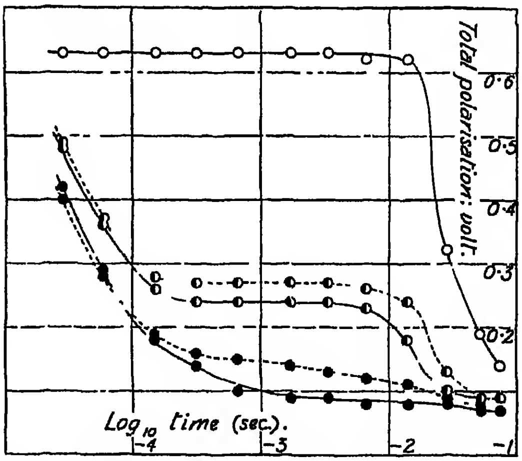

FIG. 3.—Ageing of electrode with use; 0·02 N. HCl. 0·35 amp. per sq. cm., 25°; time-decay of polarisation,
—O— Electrode A, after use in many experiments.
—◐— Electrode A, replatinised and polarised 150 min. at 0.4 amp. per sq cm. in 0·02 N. HCl at 25°.
—●— Electrode B, replatinised and kept in distilled water until used.
Dotted lines—see text.

An experiment with electrode B (kept nine weeks in distilled water) gave wholly different time-decay curves from those given by electrode A, although the polarisation—c.d. curves did not differ significantly. The behaviour of electrode B was similar to that shown by the middle pair of curves in Fig. 3, in contrast to the top curve of the same figure, which was characteristic of electrode A under the same conditions. This remarkable result led us to perform the following experiments to investigate this hitherto quite unsuspected ageing effect. Both electrodes were cleaned and replatinised by identical procedures. Electrode A was polarised in 0·02 N. HCl for 150 min. at 25° at a steady c.d. of 0·4 amp. per sq. cm. (taking the usual care to avoid any contamination by anode

products), while electrode B was put aside in distilled water. A set of polarisation measurements was then made in the same acid at 25°. The difference between the electrodes are most clearly revealed in the decay curves, those for a c.d. of 0·35 amp. per sq. cm. being shown in Fig. 3, in which the dotted lines represent a second series of measurements, after electrode A had been subjected to a further 150 min. polarisation under the same conditions, electrode B again having been put aside in distilled water. Polarisation–c.d. curves are shown in Fig. 4, the top curve having been obtained with the original electrode A, the middle one with electrode A freshly platinised and aged at 0·4 amp. per sq. cm. for 150 min., and the lower curve with electrode B freshly platinised but not aged.

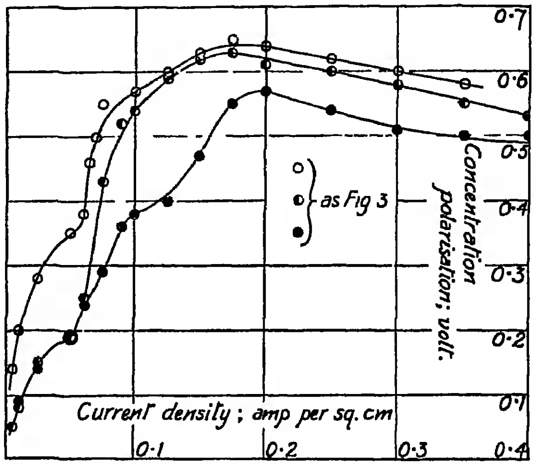

FIG. 4.—Effect of electrode ageing on polarisation; 0·02 N. HCl, 25°.

The freshly platinised electrode B shows the greatest contrast with earlier results, particularly in its very rapid time-decay without any trace of a horizontal. The aged electrode A also shows an initial rapid decay, but its decay curve now includes a horizontal part followed by a rapid fall. After polarisation for a second period of 150 min. at 0·4 amp. per sq. cm., the horizontal part is raised a few centivolts. Apparently even the small amount of use to which electrode B was put during the polarisation measurements was sufficient to raise its decay curve slightly. It is interesting to note that, after storage in distilled water for nine weeks, electrode B behaved in a very similar way to electrode A after re-platinising and ageing by 150 min. polarisation. To establish that the electrodes were not poisoned, hydrogen overvoltages in N. HCl were measured with both electrodes; these were quite normal and in agreement with the values measured by Hickling and Salt.[3]

Discussion.

These results confuse the distinction between hydrogen overvoltage and concentration polarisation. In this and earlier work, large polarisations have been observed at platinised platinum electrodes in dil. HCl; since hydrogen overvoltage, as that term is generally understood, certainly does not vary with pH to an extent which would account for such large potentials, these have previously been ascribed to concentration polarisation. However, concentration polarisation has always been regarded as an effect arising in the electrolyte independent of the nature of the electrode. The experiments on electrode ageing show that the polarisations do, in fact, depend on the state of the electrode. Thus, two electrodes which have overvoltages of the order of 0·07 v. in N. HCl at 0·35 amp. per sq. cm. show different polarisations in 0·02 N. acid (at the same c.d.) and the corresponding time-decay curves are strikingly different.

On the atomic hydrogen theory of overvoltage it might be supposed that the polarisation is due to an accumulation of atomic hydrogen on, or near, the surface of the electrode. On this theory it must be explained why a higher concentration of atomic hydrogen should be attained in dilute than in concentrated acid. The low overvoltage of platinised platinum (in N. HCl) has been explained by the high rate at which adsorbed hydrogen atoms combine together owing to the catalytic activity of the surface; this results in a low stationary surface concentration of adsorbed atomic hydrogen and hence a low overvoltage.

In dilute acids and at high c.ds. it can be assumed that the electrolyte concentration within a small distance of the electrode is very small, even approaching zero. It is probable that under these conditions the greater part of the steady polarising current is maintained by the neutralisation of oxonium ions some distance up to about 30 A. from the electrode. Neutral H_3O is more likely to decompose into atomic hydrogen and water than into molecular hydrogen and hydroxy radicals, since the O—H bond energy is a few Kcal. per mole greater than that of H_2. Some of the liberated hydrogen atoms would combine in the solution and the rest at the electrode surface. The essential point is the existence of a region near the electrode free from acid and containing an appreciable concentration of hydrogen atoms. The potential of the electrode would be negative with respect to a reversible hydrogen electrode in the body of the electrolyte as it would be acting as an atomic hydrogen electrode, the negative potential being logarithmically proportional to the activity of the atomic hydrogen and linearly proportional to the pH of the solution in contact with the electrode (the latter is probably near 7). The negative electrode potential is balanced by positive oxonium ions in a diffuse double layer situated some distance from the electrode in the region where the acid concentration begins to be appreciable.

The Mechanism of Molecular Hydrogen Formation.—It can safely be assumed that before electrolysis begins, the electrode surface is covered with an adsorbed layer of water molecules, possibly containing oxonium or chloride ions in addition. During electrolysis many of these adsorbed molecules and ions are likely to be displaced by hydrogen atoms. Adsorbed atomic hydrogen is believed to form molecular hydrogen by two mechanisms: [4]

(*a*) by surface catalysis, adsorbed atoms moving over the electrode surface until they meet and react. The surface mobility of adsorbed atomic hydrogen is, however, open to some doubt;

(*b*) by the electrochemical mechanism, $M—H+H_3O^+ + \epsilon = M+H_2+H_2O$, which is considered to be the main process when an appreciable fraction of the available surface is occupied by adsorbed hydrogen.

Whereas in concentrated acid both mechanisms may account for the formation of molecular hydrogen, in dilute acid at high c.ds. the electrochemical mechanism cannot operate owing to the absence of oxonium ions at the electrode. In this case adsorbed atomic hydrogen is probably removed by direct reaction with dissolved atomic hydrogen, a reaction likely to have a very low activation energy and therefore to be rapid. Hydrogen atoms can probably also combine in solution, the dissociation energy of hydrogen being less than that of water.

The Time-Decay of Polarisation.—During the passage of current, hydrogen atoms and water are adsorbed on the electrode, and hydrogen atoms are present in the water near the electrode. Hydrogen molecules are being formed by reaction between dissolved hydrogen atoms, by reaction between adsorbed and dissolved hydrogen atoms, and perhaps by the catalytic mechanism. There will be a stationary concentration (for constant c.d.) of adsorbed atomic hydrogen, replaced from solution as fast as removed; and a stationary concentration of dissolved atomic hydrogen, maintained by hydrogen atoms newly formed at a distance

from the electrode. The electrode potential is negative on account of the electromotive activity of the atomic hydrogen.

To find a mechanism for the discharge of the electrode when the polarising current ceases, it is necessary to consider how the electrode can lose its negative charge to the solution, or equivalently, how the double layer can collapse. The moment the externally imposed current ceases, acid ions situated at a distance from the electrode are able to migrate towards it without being neutralised. The potential of the double layer would be maintained, as it contracts, by the addition to it of more oxonium ions as hydrogen atoms lose electrons to the electrode. This is likely to occur since any fall of electrode potential would result in the ionisation of hydrogen atoms situated favourably with respect to water molecules for the formation of oxonium ions. Thus the electrode potential would tend to remain relatively constant until the double layer has contracted to a thickness of molecular dimensions and the oxonium ions can be discharged by collision with adsorbed hydrogen atoms or by the catalytic mechanism. It is difficult to form any estimate of the probable duration of such a potential decay process, as the initial conditions are not known.

Perhaps the most remarkable feature of the time-decay results is the constancy of potential for well-aged electrodes over the first $\frac{1}{100}$ sec. (at high c.ds.). Whereas this may be due to the maintenance of a balance between the charge and thickness of the double layer, it might alternatively be due to the persistence of a complete film of adsorbed hydrogen for the requisite time.

The above discussion does not interpret many features of the polarisation measurements, particularly the remarkable dependence of time-decay on the state of the electrode, but we prefer to postpone further consideration of the subject until measurements now being made with other electrode materials have been completed.

The authors wish to thank Prof. W. E. Garner, F.R.S., and Dr. D. D. Eley, for helpful discussions.

Summary.

The polarisation of platinised platinum cathodes has been measured in 0·01 to 0·05 N. HCl acid at 25°. The polarisation—c.d. curves have a maximum, and an inflexion at about 0·3 to 0·5 V.

The curves showing the time-decay of polarisation on interruption of the polarising current indicate a rather sharp transition between two types of electrode process; this transition corresponds to the inflexion in the polarisation—c.d. curves.

Freshly platinised electrodes behave differently from electrodes which have been aged by continuous cathodic polarisation. This difference is most clearly revealed in the time-decay of the polarisation at high c.d.; a fresh electrode shows a rapid initial decay to a low potential, while a much used electrode remains at a constant potential until about $\frac{1}{100}$ sec. after the interruption of the polarising current—when the potential falls very rapidly. This dependence on the state of the electrode indicates that the polarisation is not a true concentration polarisation, i.e. is not due solely to concentration changes in the solution. No satisfactory interpretation of the results has been obtained.

Résumé.

La polarisation de cathodes en platine platiné a été mesurée dans HCl de normalité 0·01 à 0·05. Les courbes de polarisation présentent un maximum et un point d'inflexion, ce dernier à environ 0·3-0·5 V. Les courbes de la dépolarisation par interruption du courant polarisant en

fonction du temps indiquent une transition entre deux types de processus à l'électrode, transition qui correspond au point d'inflexion mentionné plus haut. Les électrodes fraîchement platinées se comportent différemment d'électrodes qui ont été " vieillies " par une polarisation cathodique continue, la différence étant révélée plus clairement par la courbe dépolarisation-temps, après une polarisation à haute densité de courant. Ceci indique que la polarisation n'est pas dûe seulement aux changements de concentration de la solution, mais ces résultats n'ont pas encore été interprétés de manière satisfaisante.

Zusammenfassung.

Die Polarisation von platinierten Platinelektroden wurde in 0·01-0·05 N. HCl bei 25° C. gemessen. Die Polarisations—Stromdichtekurven weisen ein Maximum und bei 0·3-0·5 V. einen Wendepunkt auf.

Die Kurven, die den zeitlichen Verlauf der Abnahme der Polarisation nach Unterbrechung des Polarisationsstroms darstellen, deuten auf einen plötzlichen Übergang zwischen zwei Arten von Elektrodenvorgängen hin. Dieser Übergang entspricht dem eben erwähnten Wendepunkt.

Frisch platinierte Elektroden verhalten sich anders als Elektroden, die durch andauernde kathodische Polarisation gealtert worden sind, was sich besonders deutlich am zeitlichen Verlauf der Polarisationsabnahme bei hohen Stromdichten zeigt. Es folgt hieraus, dass die Polarisation nicht nur duich Konzentrationsveränderungen in der Lösung verursacht wird. Eine befriedigende Erklärung dieser Resultate ist bisher nicht geglückt.

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ELECTROCHEMICAL PERIODICITIES IN THE ANODIC POLARISATION OF PLATINUM ELECTRODES IN THE PRESENCE OF HYDROGEN AND THEIR SIGNIFICANCE.

BY G. ARMSTRONG AND J. A. V. BUTLER.

Received 10*th April*, 1947.

The available evidence, which has been reviewed elsewhere,[1] suggests that there is no single process for the cathodic liberation of hydrogen, which is applicable at all electrodes. It is probable that most of the processes which are theoretically possible may occur at one or other electrode, the one which actually occurs being naturally that which has the greatest rate in the circumstances. It is a matter for experiment to discover which process actually occurs in a given case.

The possible processes may be listed, perhaps not very accurately, as follows.

(1) Discharge of hydrogen ions, giving free hydrogen atoms which are not appreciably adsorbed on the electrode, and combine with each other to form molecular hydrogen:

$$H^+ + e = H ; \; H + H = H_2.$$

[1] See the author's *Electrocapillarity : The Chemistry and Physics of Electrodes and other Charged Surfaces*. Ch. VI. (Methuen, 1940.)

Gurney [2] in his well-known quantum-mechanical treatment investigated the condition under which hydrogen ions (H_3O^+) are neutralised to free hydrogen atoms.

(2) The hydrogen ions give rise on neutralization to hydrogen atoms, adsorbed on the electrode,[3] which process may be represented as follows:

$$H^+ + M + e = M - H$$

There now follow a number of possibilities.

(*a*) The adsorbed hydrogen can be desorbed as H_2 at a rate equal to its rate of deposition:

$$\begin{matrix} MH^+ \\ MH^+ \end{matrix} \rightleftharpoons \begin{matrix} M - H \\ M - H \end{matrix} \rightleftharpoons \begin{matrix} M \\ M \end{matrix} + H_2.$$

(*b*) The rate of desorption from the electrode surface, even when saturated with hydrogen is less than the rate of formation of neutral hydrogen. The metal will then be completely covered with adsorbed hydrogen and some other process must come into operation, such as

(α) The discharge of hydrogen ions to form free hydrogen atoms, similar to process (1), except that it now occurs at a surface covered with adsorbed hydrogen rather than at the uncovered metal. Molecular hydrogen is formed by the union of two such free atoms:

$$(M—H)H^+ + e \rightarrow H\,;\ 2H = H_2$$

(β) Molecular hydrogen is formed by the combination of a free hydrogen atom with an adsorbed hydrogen atom. Various mechanisms have been suggested, e.g.

$$\begin{aligned} M—H \ + H^+ + e &= M + H_2{}^{5} \\ M—H^- + H^+ \quad &= M + H_2{}^{6} \end{aligned}$$

(γ) A second layer of more loosely attached adsorbed hydrogen is formed, in which molecular H_2 formation can occur more readily:

$$\begin{matrix} M - H \ldots . H \\ M - H \qquad\quad \\ M - H \ldots . H \end{matrix} \rightarrow \begin{matrix} M - H \\ M - H + H_2 \\ M - H \end{matrix}$$

There are no doubt other possibilities, and other ways in which they could be formulated, but the decision as to what happens at a particular electrode must be an experimental one. It is necessary to seek to discover the amount and state of the adsorbed, or otherwise attached, hydrogen at the electrode. The practical methods available at present for obtaining this type of information are rather limited. They may be listed as follows.

(1) The polarisation curves (electrode potential-time), during the formation (cathodic) of hydrogen at the electrode, or the ionization (anodic) of hydrogen previously deposited, may help to distinguish the process occurring.[6]

(2) The decay of electrode potential with time at open circuit will indicate the existence of electromotively-active products.[7]

(3) The deuterium-hydrogen separation factor differs for the various processes and may enable them to be distinguished.[8]

All the evidence obtained in these ways cannot be reviewed here.

[2] Gurney, *Proc. Roy. Soc. A.*, 1931, **137**, 132.

[3] Butler, *Trans. Faraday Soc.*, 1932, **28**, 379. Hammett, *ibid.*, 1933, **29**, 770. Erdey-Gruz and Volmer, *Z. physik. Chem. A.*, 1930, **150**, 203. Butler, *ibid.*, 1936, **157**, 432.

[4] (*a*) Horiuti and Okamota, *Sci. Pap. Ist. Physic. Chem. Res., Japan*, 1936, **28**, 231.

(*b*) *Bull. Chem. Soc., Japan*, 1938, **13**, 216, 228.

[5] Heyrovski, *Rec. Trav. Chim.*, 1925, **44**, 499; 1927, **46**, 528; *Coll. Czech. Chem. Comm.*, 1937, **9**, 273, 345.

[6] Bowden, *Proc. Roy. Soc. A.*, 1929, **125**, 446; Butler and Armstrong, *ibid.*, 1932, **137**, 604; 1933, **143**, 89.

[7] Armstrong and Butler, *Trans. Faraday Soc.*, 1933, **29**, 1261.

[8] Horiuti and Okamota, ref. (4*a*); Butler, *Z. Elektrochem*, 1938, **44**, 55.

It may be mentioned, however, that at mercury electrodes a careful examination [9] did not reveal any deposition of adsorbed hydrogen at potentials below the normal overvoltage, and the decay of the hydrogen overvoltage does not reveal the presence of hydrogen in any " active " form, unless it is quite short-lived. Probably mechanism (1) is adequate for mercury and similar high overvoltage metals.

On the other hand, at *reversible* hydrogen electrodes there is clearly a mobile equilibrium between hydrogen ions on the one hand, and molecular hydrogen dissolved in the solution on the other. If both anodic and cathodic processes can occur without a very great displacement of the potential from the reversible value, it is evident that the electrode process is of the type 2*a*.

As is well-known, this reversible process occurs very readily at platinized electrodes, but it has been known for a long time that *bright* platinum electrodes can also be brought into a state in which they exhibit reversibility.[10] This type of activation of the electrodes can usually be brought about by anodic polarisation in the presence of dissolved hydrogen. Usually electrodes which have been activated in this way, gradually lose their activity on standing. Since it has been shown that the deposition of impurities, such as arsenic,[11] on the electrode destroy the activity, it may be inferred that the " activation " process consists in removing foreign material, although there may be other factors involved.[12]

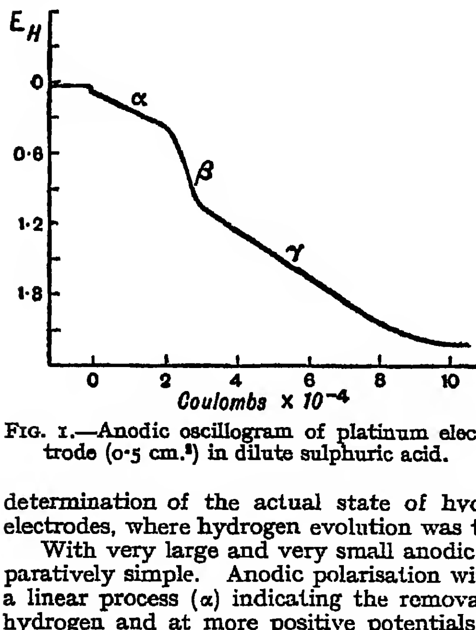

FIG. 1.—Anodic oscillogram of platinum electrode (0·5 cm.²) in dilute sulphuric acid.

The phenomena to be described were encountered in the course of a long series of experiments which had as their object the determination of the actual state of hydrogen at platinum and other electrodes, where hydrogen evolution was taking, or had taken, place.

With very large and very small anodic currents the behaviour is comparatively simple. Anodic polarisation with large currents (Fig. 1) shows a linear process (α) indicating the removal of a single layer of adsorbed hydrogen and at more positive potentials, the deposition in its place of adsorbed oxygen.[13] With very small currents the potential may stay indefinably near the reversible hydrogen potential, molecular hydrogen diffusing up to the electrode to replace that used up. However, as indicated above, the electrodes usually gradually lose their activity under these conditions and after a time the potential can no longer be maintained near the reversible hydrogen value.

With intermediate anodic currents very complicated phenomena occur. If the electrode is active to begin with, the potential remains at first near the reversible hydrogen value (Fig. 2*b*), but if the hydrogen is used up

[9] Barclay and Butler, *Trans. Faraday Soc.*, 1940, 36, 128.

[10] Beans and Hammett, *J. Amer. Chem. Soc.*, 1925, 47, 145; Hammett, *ibid.*, 1924, 46, 7; Hammett and Lorch, *ibid.*, 1933, 55, 70; Bowden, *Proc. Roy. Soc. A*, 1929, 125, 446; Butler and Armstrong, *J. Chem. Soc.*, 1934, 743.

[11] Volmer and Wick, *Z. physik. Chem. A*, 1935, 172, 429.

[12] Armstrong and Butler, *J. Chem. Soc.*, 1934, 743.

[13] *Loc. cit.*,[12] also Pearson and Butler, *Trans. Faraday Soc.*, 1938, 34, 1163; Barclay and Butler, *loc. cit.*[9]

near the electrode faster than it is replenished by diffusion, the potential eventually falls and becomes steady again at about + 0·4 v. It is obvious that an alternative anodic process is encountered here. Since the potential is still too negative for the deposition of oxygen (which begins at about + 1·0 v.) and the process at + 0·4 v. is too lengthy to be accounted for as the deposition of impurities from the solution; it must be an alternative process for the ionization of hydrogen. It has been shown that the source of the hydrogen in this case is that dissolved in the electrode metal.[13]

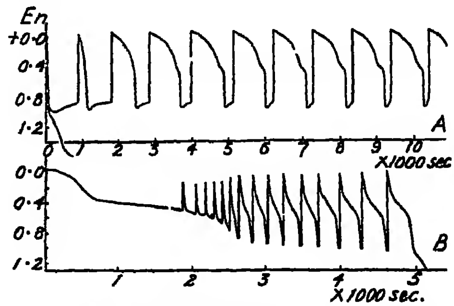

FIG. 2.—Anodic polarisation of bright platinum electrodes in dilute sulphuric acid saturated with hydrogen.

A, current, 62×10^{-7} amp.; B, current,

At this point a long series of periodic changes may occur in which the potential oscillates between the reversible value 0·0 and the alternative value 0·4 v. The interpretation of this phenomenon is that when the alternative process begins it gives an opportunity for the molecular hydrogen to reach the electrode again by diffusion and so re-establish the reversible potential. After a considerable number of these oscillations the electrode loses its activity. It can no longer return to the reversible potential and the potential falls to more positive values at which oxygen is deposited. However, sometimes the electrode becomes reactivated at this point and the potential may rise once again to the reversible value, followed by the whole series of periodicities, like Fig. 2*b* again. It may, however, fail to become reactivated and the potential will then remain permanently in the oxygen region.

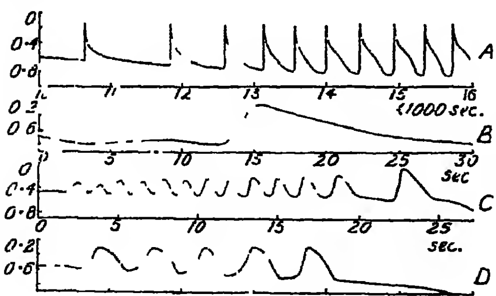

FIG. 3.—Anodic polarisation of bright platinum electrodes in hydrogen atmosphere.

A, $5{\cdot}5 \times 10^{-7}$ amp.; B, 290×10^{-7} amp.; C, 880×10^{-7} amp.; D, 7630×10^{-7} amp.

In the second type of periodicities the electrode is not originally active (Fig. 2 *a*). In its first anodic polarisation, the potential falls at once into the oxygen region. This gives it some slight activity and the second time some hydrogen ionization occurs between 0·0 and 0·6 v. and the electrode becomes activated at about 0·8 v. In this series the electrode becomes more active and the amount of hydrogen ionized in each "period" increases, but the ionization process occurring at + 0·4 remains short and is never as fully developed as in example 2*b*. The reason for this is probably the small amount of hydrogen dissolved in the electrode.

Other types of periodicities have also been observed. In the series shown in Fig. 3*a* the periodicities began only after a very long period of anodic polarisation (> 10,000 sec.). Once begun they are of the same type as those of Fig. 2*b*. With larger currents the periodicities have a much shorter period and lose their characteristic shapes. Fig. 3 (*b*), (*c*) and (*d*)

are examples obtained with an Einthoven tring galvanometer, with comparatively large currents.

To sum up, the experiments indicate that there are two distinct processes whereby the ionization of hydrogen occurs at the same platinum electrode and oscillations, determined by the mechanics of diffusion, may occur from the one to the other. Since there are two distinct processes, with potentials differing by 0·4-0·5 v., the energy of bonding of the hydrogen to the electrode must differ correspondingly. Thus, if the process near the reversible potential involves adsorbed hydrogen, that at + 0·4 v. involves hydrogen more firmly bound to the electrode by about 10,000 cal. Since oscillations occur between these two processes, the electrode remains active, i.e. capable of exhibiting the reversible hydrogen electrode potential if sufficient hydrogen is present. The gradual loss of this activity is, however, a distinct phenomenon and may be due to the deposition of impurities on the electrode since reactivation occurs at about + 1·0 v., at which such impurities may be removed or oxidised. It is significant that the deposition of oxygen on the electrode begins at this point, and it is quite possible that this oxygen plays a necessary part in the re-activation process.

Résumé.

Pour déterminer l'état de l'hydrogène aux électrodes de Pt, des expériences ont été faites sur leur polarisation anodique. Les résultats obtenus à hautes densités de courant montrent l'existence d'une couche atomique d'hydrogène adsorbé. Avec des densités de courant inférieures, la quantité d'hydrogène ionisable est considérablement plus grande et doit être en partie dûe à de l'hydrogène diffusant de la solution et de l'intérieur du métal vers l'interface. Avec de faibles densités de courant, on observe, aux électrodes actives, des changements de potentiel périodiques très complexes, dûs partiellement à la périodicité de la diffusion de l'hydrogène de la solution et partiellement au fait que l'électrode devient graduellement inactive, puis active à nouveau, quand le potentiel de dépôt de l'oxygène est atteint. L'inactivation a probablement pour cause le dépôt d'impuretés métalliques sur l'électrode, tandis que le processus d'activation correspond à leur déplacement.

Zusammenfassung.

In einem Versuch, den Zustand des Wasserstoffs an Pt-Elektroden aufzuklären, wurden Messungen der anodischen Polarisation solcher Elektroden unternommen. Versuche bei hohen Stromdichten zeigen die Gegenwart einer atomdicken Schicht von adsorbiertem Wasserstoff, während bei niedrigeren Stromdichten die Menge an ionisierbarem Wasserstoff weitaus grösser ist und zum Teil auf Wasserstoffdiffusion von der Lösung her oder aus dem Innern des Metalls zurückzuführen sein muss. Bei sehr kleinen Stromdichten und aktiven Elektroden treten sehr komplizierte periodische Potentialveränderungen auf, deren Ursprung zum Teil in Periodizitäten in der Wasserstoffdiffusion aus der Lösung und zum Teil in der langsamen Inaktivierung der Elektrode und Wiederherstellung der Aktivität nach Erreichung des Sauerstoffabscheidungspotentials zu liegen scheint. Die Inaktivierung wird wahrscheininlich durch die Abscheidung von metallischen Verunreinigungen an der Elektrode verursacht und die Wiederaktivierung durch deren Entfernung.

GENERAL DISCUSSION

Dr. A. Hickling (*Liverpool*) said: All the supporters of the slow-discharge theories of hydrogen overvoltage seem to make the basic assumption that the relation between overvoltage and c.d. is accurately given by the Tafel equation $\eta = a + b \log I$, and that this equation is valid no matter how high is the c.d. As was demonstrated by Salt and myself some few years ago, this equation breaks down for some metals at high c.d.'s, and there is a fairly general tendency for the overvoltage to approach a constant maximum value in each case. This clearly indicates the approach of some limiting saturation state, and the onset of a new depolarisation process at high c.d.'s, and a study of the decay of hydrogen overvoltage confirmed this conclusion. The overvoltages recorded in this work were obtained by an interrupter method, in which the measured values were extrapolated graphically to zero time of interruption, and Frumkin has adversely criticised these results in the case of mercury on the grounds that the extrapolation was in error. Frumkin's criticism, however, failed to take any account of metals other than mercury, some of which were found to obey the Tafel equation in the c.d. range explored, while others showed a marked deviation from it; it is difficult to see how any general error in the extrapolation method could account for this variety of results. Furthermore, the matter has recently been re-investigated by Bockris using the direct method of measurement, in which no question of extrapolation arises and in which any error is likely to be in the direction of making the measured overvoltages higher than the true values, and his results confirm the behaviour noted by Salt and myself. It seems, therefore, that the approach to a constant maximum overvoltage at high c.d.'s in some cases must be accepted as a genuine phenomenon, and I would emphasise that the slow discharge theories give no indication whatever that this behaviour is to be expected whereas it meets with a ready explanation on the atomic hydrogen view.

Weiss has ingeniously shown that by making certain assumptions it is possible to derive values of the constant b in Tafel's equation of 0·058, 0·116, and 0·23 at 20° C., assuming that the neutralisation of the hydrogen ion is the rate-determining stage in the electrode process. I would point out that the experimental values of b range from 0·02 to 0·3 and that there is no real correlation with these calculated values. Furthermore, the most important phenomenon in hydrogen overpotential is its dependence upon the nature of the cathode material, as given by the constant a in Tafel's equation. No unequivocal statement of what determines the value of a appears to be given by supporters of the slow-discharge theories although it is of far greater intrinsic interest than the value of b. It must presumably depend in some way, on the slow-discharge view, upon the thermionic work function of the metal, and a simple view would suggest that where this is high, a and therefore the overpotential should also be high. Actually, as the results of Bockris show, the converse is the case. On the atomic hydrogen theory of overvoltage, the influence of the cathode material receives a plausible interpretation in terms of the experimentally ascertained catalytic powers of the surfaces on the combination of hydrogen atoms.

With reference to Agar's paper on the interpretation of overpotential measurements in terms of activation energies, I am not at all convinced that this mode of treatment is particularly valuable in arriving at a satisfactory theory of overvoltage. Obviously if we have any rate process which is temperature dependent we can by analogy with ordinary chemical reactions calculate a quantity which we can call the heat of activation. But what then? Surely this is not an end in itself. For any satisfactory theory of overvoltage we must identify the slow stage in the total electrode reaction, and be enabled thereby to make detailed

predictions of the influence of experimental variables on overvoltage. I cannot see that the activation mode of treating the experimental data assists greatly in this respect.

In connection with Bowden and Grew's paper on the capacity of the double layer at mercury in acid solution, I would suggest that the value of 20 μF./sq. cm., which tends now to be unquestioningly accepted, is probably rather too high. Since Frumkin pointed out that contamination of the mercury surface greatly decreased the capacity, there has been a marked tendency to dismiss all lower values as being in error due to this cause. Grahame in 1941, in what is probably the most thorough study of the double layer capacity yet made, obtained a value of 16 μF./sq. cm. In my own laboratory we have made some scores of measurements using both a D.C. oscillographic method and an A.C. method with both liquid mercury and amalgamated electrodes, and over a period of 7 years different workers have consistently obtained a value of 12 ± 1 mfd./sq. cm. for the minimum capacity in N. H_2SO_4 immediately prior to hydrogen evolution; occasional drops to much lower values have been noted when contamination of the surface occurred.

Dr. D. D. Eley (*Bristol*) said: Chemisorbed hydrogen atoms are supposed to play a part in most theories of the discharge of hydrogen. Horiuti and Hickling, for example, suppose that on catalytically-active metals, the recombination of chemisorbed atoms and evaporation of hydrogen molecules proceeds rapidly:

$$2M - H \rightarrow M \ldots H_2 \qquad (1)$$
$$M \ldots H_2 \rightarrow M + H_2$$

where M is a surface metal atom.

On catalytically-inactive metals the hydride surface film M—H is supposed to be relatively stable, and the discharge to involve the electrochemical mechanism:

$$e + M - H + H_3O^+ \rightarrow M + H_2 + H_2O \qquad (2)$$

Modern work emphasises the essential *stability* of chemisorbed hydrogen on metals *in vacuo*. J. K. Roberts [1] initiated this work when he showed that a clean tungsten surface would instantly chemisorb a monatomic layer of hydrogen which was relatively stable in that it only started to evaporate *in vacuo* at 500° C. Nickel and other metals behave similarly.[2] These surface hydrides are very catalytically active in the parahydrogen conversion.[3, 4] Mercury, generally regarded as a catalytically-inactive metal, when cleaned free from oxygen also adsorbs a stable layer of hydrogen atoms.[5]

In other words, there is considerable evidence that reaction (1), desorption of chemisorbed hydrogen, does not occur at an appreciable rate *in vacuo* at room temperature, on several metals of different type. For tungsten the heat of desorption is 18-45 kcal., depending on the fraction of surface covered.[1]

How far this desorption energy may be lowered at an electrode by interaction of the electrical field of the double layer with the M — H dipole is purely a matter of speculation at present. When attempting to make such a calculation some years ago,[6] I found the main difficulty to be the "siteing" of the M—H dipole in the double layer.

In considering the desorption of such tightly bound layers, there is always also the possibility of a displacement desorption, e.g.

$$H_2O + 2M - H \rightarrow 2M - H_2O + H_2 \qquad (3)$$

[1] Roberts, *Some Problems in Adsorption* (Cambridge, 1939).
[2] Beeck, Smith and Wheeler, *Proc. Roy. Soc. A*, 1940, **177**, 62.
[3] Eley and Rideal, *ibid.*, 1941, **178**, 429; Eley, *ibid.*, 452.
[4] A. and L. Farkas, *J. Amer. Chem. Soc.*, 1942, **64**, 1594.
[5] Burdon, *Proc. Physic Soc.*, 1935, **47**, 460.
[6] *Ph.D. Thesis* (Manchester, 1937).

where we do not specify the nature of chemisorbed water, since it is not known. How far such a displacement can occur is still not clear. The parahydrogen conversion on platinum is poisoned by water vapour.[7] Such conversions, however, probably proceed by an exchange between chemisorbed and van der Waals' adsorbed hydrogen,[8] viz.,

$$M - H \ldots D_2 \rightarrow M - D \ldots HD \quad . \quad . \quad (4)$$

When the poisoning action of water is reversible, it may only be displacing hydrogen from the van der Waals layer, and not the chemisorbed layer.

The work of Bonhoeffer [8] on the catalysed recombination of hydrogen atoms by metals forms a salient point in discussions of hydrogen overvoltage. He pointed out that the series of decreasing catalytic efficiency, viz.: Pd, Pt, Ag, W, Fe, Cu, Ca, Pb, Hg, was the order of their increasing "hydrogen overvoltage." However, it is rather unlikely that hydrogen atoms in the temperature range of interest recombine according to (1), i.e.

$$2H + M \rightarrow 2M - H \rightarrow 2M \ldots H_2 \rightarrow 2M + H_2 \quad . \quad . \quad (5)$$

It is much more likely that the hydrogen layer is fairly full at temperatures up to 500° c. and that recombination occurs by an atom from the gas striking a chemisorbed atom and evaporating as a molecule.

$$H + M\text{—}H \rightarrow M + H_2. \quad . \quad . \quad . \quad . \quad (6)$$

This mechanism is then the reverse of that shown to hold for the production of hydrogen atoms by hot tungsten.[9] The work of Roginski and Schechter is of interest in this connection.[10]

To summarise, then, I would say that the evidence on chemisorbed hydrogen on clean metals *in vacuo* would lead one to suspect mechanisms employing the recombination of loosely chemisorbed hydrogen atoms and to favour mechanisms based on a largely complete, strongly bound hydrogen layer, such as the electrochemical mechanism (2), or mechanisms such as (6), where the H atom is produced in the solution by an electron transfer from the electrode, as suggested by Bryant and Coates to this meeting.

I would further note that steps such as (2) and (6) may proceed in the reverse direction in the case where a certain number of gaps exist in the chemisorbed layer. There are various reasons why such gaps may exist.[1]

How far a metal surface in an electrochemical experiment can ever be "clean" is another question. Initially, there will be at least a monatomic oxide layer on the surface of the metal, apart from the possibility of poisoning by tap grease, mercury vapour, etc.

Prof. N. K. Adam (*Southampton*) (*partly communicated*): Slow electron transfer from the cathode to the hydrogen ion seems to me to be assumed without adequate evidence. Electron transfer, in itself, does not appear to be usually a slow process, for a great many electrode reactions, including redox electrodes and metals in solutions containing their own ions, are reversible, without any marked overpotential. It would appear more reasonable to seek the cause of hydrogen overpotential in some special property of hydrogen or its ion than to assume that the electron transfer is slow in this particular case, when it is not slow in so many other cases.

We know that hydrogen forms a very stable adsorbed layer on many metals. Weiss apparently prefers to assume that the oxonium ion H_3O^+

[7] A. Farkas, *Trans. Faraday Soc.*, 1936, **32**, 922; A. and L. Farkas, *ibid.*, 1937, **33**, 678.

[8] Bonhoeffer, *Z. physik. Chem.*, 1924, **113**, 199.

[9] Roberts and Bryce, *Proc. Camb. Phil. Soc.*, 1936, **32**, 653; Bosworth, *ibid.*, 1937, **33**, 394.

[10] Roginski and Schechter, *Acta Physicochim.*, 1934, **1**, 318; Schechter, *ibid.*, 1939, **10**, 379.

is adsorbed, but surely that is far less likely to be strongly adsorbed than H^+. Frumkin says that the capacity of the double-layer remains nearly constant at 20 μF./cm.^{2}, from low to high c.d.'s, and deduces from this that adsorbed hydrogen *atoms* are not present on the mercury cathode, stating that their appearance would cause a considerable increase in the electrode capacity. I am not quite clear why the appearance of adsorbed hydrogen should greatly increase the electrode capacity; but if it does, the constant capacity could alternatively be explained on the hypothesis (a quite probable one) that the layer of adsorbed hydrogen is practically complete at extremely low c.d.'s. It is well known that the capacity of anodic mercury is 2-4 times larger than the 20 μF./cm.^{2} of cathodic mercury. Possibly the adsorbed films do strongly affect the capacity, a capacity of 20 μF./cm.^{2} being characteristic of a hydrogen-covered surface, one of 40 to 80 μF./cm.^{2} characteristic of an oxygen-covered surface.

Unless it can be shown why the electron transfer is much slower with hydrogen ion and electrodes of most metals than with "reversible" electrodes, I am reluctant to accept the view that slow electron transfer is the cause of overpotential. The slow stage may well be later; either the slow combination of hydrogen atoms, suggested by Tafel and favoured by many later writers, or the mechanism mentioned by Eley above,

$$MH + H_3O^+ + e \rightarrow M + H_2 + H_2O,$$

MH being an adsorbed layer of hydrogen atoms. The very marked effect of arsenic and other catalyst poisons in increasing overpotential is evidence for the importance of adsorbed hydrogen films in creating overpotential; if it could be shown that arsenic was effective in amounts which merely hindered catalytic combination of hydrogen atoms, but still permitted their adsorption, that would be evidence for the slow stage being catalytic combination.

Dr. M. Haissinsky (*Paris*) said: In criticising the theory of the slow discharge as origin of the hydrogen overvoltage, it is not sufficient to make reference only to Gurney's theory. It was shown, by Frumkin and others, that Gurney has neglected the adsorption energy of the hydrogen on the cathode. The presence of organic molecules can of course modify the state of the electrode surface and have an effect on the adsorption energy and hence on the overpotential.

Dr. J. A. V. Butler (*London*) said: I should like to advocate, as I have been doing for the last fifteen years, that there is not just one mechanism of overvoltage, but several. There are two demonstrably different phenomena, viz. those at high overvoltage and low overvoltage electrodes, and there are quite probably others. I listed some of the possibilities in my paper. The task of research is to discover which applies in any particular case.

If I may amplify what I said previously in introducing my paper, it seems to me that the existence of a "free" hydrogen atom for any appreciable time is very improbable. Hydrogen when formed will be adsorbed in some way on the electrode and the main question is to distinguish the possible modes of adsorption and the ways in which such adsorbed hydrogen can be released. I agree with almost all Dr. Eley has said. If hydrogen is powerfully held by adsorptive forces, how is it that it comes off so easily? I think the modes of adsorptive need better definition. One might suggest that there are two factors to be considered: (1) the strength of the binding, i.e. the depths of the energy troughs in which the hydrogen atoms lie; (2) the height of the barriers between adjacent troughs. If the barriers are low the combination of the H atoms to form molecules may be easy, in fact a mobile equilibrium between H_2 molecules (held by van der Waals forces) and H atoms may be possible. This is required for the functioning of the reversible hydrogen electrode. I should also like to see a study of the adsorption of hydrogen

in a second layer, i.e. when the first layer is completed; and the properties of hydrogen held in this way.

The second point I should like to bring up is to ask Dr. Agar if he has any new values of the activation energies of hydrogen-discharge reactions. It may be remembered that some years ago Eyring, Glasstone and Laidler [11] found that if the known values of ΔH are inserted in the equation $i = B\,e^{-\Delta H/RT}$, the constant B comes out about the same in both alkaline and acid solutions. They drew from this the conclusion that the hydrogen ions are not directly implicated in the discharge process, the molecule concerned being, in fact, water. I do not think this conclusion was justified, for it is based on a calculation which involved the assumption that the hydrogen ion concentration in alkaline solutions is independent of the temperature. If we allow for the change of $[H^+]$ in alkaline solutions at constant $[OH^-]$, I have shown that the equation $i = B[H^+]\,e^{\;\Delta H/RT}$ fits the rather limited facts equally well.[12] But there is great need for more data, which will permit a better analysis.

It has been asked if there is any explanation of the order of magnitude of these activation energies, actually observed. I think I have shown that a figure of the order of 20 kcal. is not an unreasonable one for the formation of a free hydrogen atom, and if the latter is adsorbed some reduction may be expected.[13] In alkaline solutions the comparable figure is about 9 kcal. This can be explained by taking into account the facts that (1) the reversible electrode potential is 0·7 v. more negative; this will reduce the activation energy by about half this amount, or 8 kcal. Furthermore the proton is at an energy level about 14 kcal. lower in H_2O (the actual acid in alkaline solutions), than in H_3O^+. This will produce a further lowering of the activation energy, the amount depending on the shape of the potential energy curve. The actual value of 9 kcal. is thus of the order to be expected.

Dr. J. O'M. Bockris (*London*) (*partly communicated*): Prof. Ferguson's paper appears to be of particular value to overvoltage research at the present time because of the original attitude taken in it. With regard to the questions 6 and 7 at the beginning of his paper, it appears from recent work on hydrogen overpotential in mixed aqueous-non-aqueous solutions [14] that hydration has no primary effect on overpotential because, for example, in ethyl alcohol-water mixtures, the variation in overvoltage with solvent composition at a given c.d. in no way follows the variation of the solvation of the hydrogen ion in that solvent.[15] The outstanding point to stress, however, is the manner in which change in solvent composition can affect different electrode materials in quite different ways, tending to support the contention that the effect originates in a solvent layer bound to the cathode in a manner characteristic of the latter.

Analogously to Prof. Ferguson's report of underpotential on platinised platinum cathodes, the present author has observed discharge of hydrogen at potentials more positive than the reversible value at Ta and (with R. Parsons) at Pd cathode at 10^{-3} amp./sq. cm. (N. HCl_{aq} solution). After some minutes' electrolysis these became overpotentials and it seems only possible to explain such a behaviour upon the grounds of the reduction, in the early stage of the electrolysis, of the surface concentration of hydrogen by diffusion into the metal.

The *general* diffusion theory of overpotential advocated by Prof. Ferguson seems weak from the view point of activation energy, that in diffusion processes being of a different order from that in overpotential.[16]

[11] *J. Chem. Physics.*, 1939, 7, 1053; 1941, 9, 91.
[12] *Ibid.*, 1941, 9, 279.
[13] *Proc. Roy. Soc. A*, 1936, 157, 423.
[14] Bockris, *Nature*, 1946, 158, 584.
[15] Goldschmidt, *Z. physik. Chem.*, 1914, 89, 129.
[16] Eyring, Glasstone and Laidler, *The Theory of Rate Processes* (1940).

With regard to Hickling and Salt's theory of hydrogen overpotential,[17] described in the paper of Bryant and Coates, it appears necessary to point out that an exact physical meaning does not seem to be attachable to the theory. If one calculates the number of hydrogen atoms setting up the pressure of atomic hydrogen which determines the cathode potential, assuming the gaseous atmosphere to exist up to about 10 A. from the cathode surface, one finds it to be less than one atom for the metals of higher potential. This difficulty presumably means that the pressure of gaseous atomic hydrogen over the electrode in the theory cannot be accepted literally but must be a measure of some more fundamental property of the individual atoms. The situation appears analogous to the interpretation of the physically impossible values of solution pressure in Nernst's theory of the e.m.f. Qualitatively, also, it appears difficult on this theory to form a physical picture of conditions at the cathode in the vicinity of which there is supposed to be a continuous layer of gaseous hydrogen; the mechanism of ion transport through this layer does not seem clear.

The theory is very helpful, however, in a qualitative way. Thus, important evidence in its favour consists in the approach towards a limiting value of overvoltage found by Hickling and Salt [18] at high c.d.'s for certain cathodes, e.g. Pb and Sn. Frumkin [19] criticised this on the grounds of an incorrect extrapolation in the commutator method used. It seems cogent to record that the present author,[20] using the direct method, has also obtained the same approach to saturation as noted by Hickling and Salt and similar approaches to saturation on other metals. As the errors of the direct method would tend to the reverse errors to that of Hickling, this seems a striking proof of the reality of the effect in solutions prepared in the way described.

With regard to the maxima on the polarisation-c.d. curves of Bryant and Coates, is it possible that these represent the effect of bubble evolution from the cathode on the thickness of the diffusion layer? With increasing c.d. the stirring effect of bubble evolution would be expected to increase and this may overcome the normal increase of concentration polarisation with c.d.

Although Dr. Weiss's paper represents a welcome attempt to correct one of the major shortcomings of Gurney's theory, it is submitted that it suffers from an important disadvantage common to Gurney's theory in that it does not give a basis to the connection between electrode material and overvoltage. One might at first think that the connection could be made through the work function. Dr. Weiss considers that the appropriate values here are those modified by the presence of adsorbed material on the electrode and this is contrary to the view of Fowler [21] who, referring to Gurney's theory, stressed that they were to be taken as those of the pure metal. It seems logical to argue, however, that in the quantum mechanical theories the work function cancels out at another part of the circuit. No simple relation between the work function of the pure metal and overpotential would hence be expected to exist from Weiss's theory. On the other hand it is an experimental fact [22] that a quite simple type of relation exists (see Fig. 1). From Fig. 1 it is clear that, exhibiting both work function and overpotential (at 10^{-3} amp./sq. cm. in aq. solution) against atomic number, then, on passing from one element to another, an increase of work function corresponds to a decrease in overpotential, which is contrary to Weiss's theory.

Further, in Dr. Weiss's treatment of the b values, no apparent explana-

[17] Hickling and Salt, *Trans. Faraday Soc.*, 1942, 38, 474.
[18] *Trans. Faraday Soc.*, 1940, 36, 1224.
[19] *Acta Physicochim.*, 1943, 18, 23.
[20] *Trans. Faraday Soc.* (in press).
[21] *ibid.*, 1932, 28, 371.
[22] Bockris, *Nature*, 1947, 159, 539.

tion of a b value $< 0{\cdot}05$ appears, though these are well known (platinised Pt, etc.).

Prof. Frumkin omitted to mention, when referring to the work of Dolin and Ershler [23] on the phenomena at Pt in H_2SO_4 and NaOH, that the rate of discharge of hydrogen atoms was found to be 27 and 11 times faster respectively than the overall rate of evolution of hydrogen. It does not seem as though, in view of this result, slow discharge of hydrogen can be still envisaged as the limiting stage at platinum. It is of great interest to observe that Prof. Frumkin is now willing to concede the importance of the combination mechanism in the cases of metals such as Pd and Ni. But it is now by no means clear why it is necessary to consider the slowness of this stage " adding " to that of the discharge mechanism. There seems

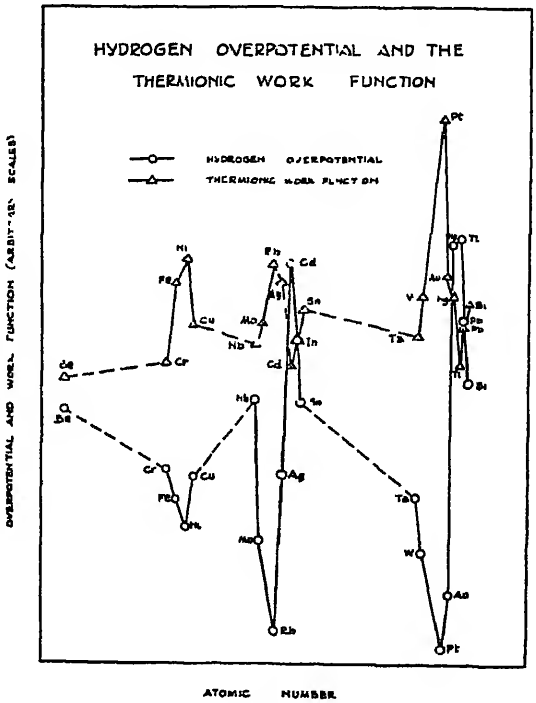

FIG. 1.

no need to consider that more than *one* of the stages governs overvoltage and for the low overvoltage metals at least there is now some balance of evidence in favour of that being a slow combination.

The results of measurements of overvoltage in the system hydrogen chloride in pyridine, in Bowden and Grews' papers, are rather obscure because reduction of the solvent very probably takes place during electrolysis. With regard to the lack of parallelism between dielectric constant of the medium and capacity of the double layer, any possible parallelism might perhaps have been expected to be vitiated in the systems chosen for examination which contain three different anions and solutes all at different concentrations.

The corrected value now reported for the capacity of the double layer prompts the question as to the comparison between the overvoltages

[23] *Acta Physicochim.*, 1940, 13, 747.

obtained in the purer solution and those in the impure solutions used by Bowden and Rideal in earlier work.[24]

In reply to Prof. Wynne Jones and Dr. Haissinsky, I do not think that one can be so pessimistic in general towards an examination of solvent effects as Prof. Wynne Jones. Every phenomenon must surely be considered individually and in the case of hydrogen overpotential, as the medium of the hydrogen ion is so much emphasised in some recent theories,[25] results from an examination of the solvent effect seem of the greatest interest. It has, in fact, offered quite unambiguous evidence against the reaction rate and quantum mechanical theory of overpotential. As to the difficulty of hydrolysis, this has been examined [26] in the cases of all the alcohols used and has been found to be undetectable within 24 hr. of making up the solutions; measurements were always made within this time. Further, extrapolated measurements to 100 % non-aqueous from measurements in mixed aqueous-non-aqueous solutions agreed to within the experimental error.

I agree with Dr. Haissinsky that by taking into account adsorption it might not be impossible to bring the results on the solvent effect into accord with the slow discharge theories. But to do this one would have to conclude that the adsorption energy was overwhelmingly more important than the solvation energy, which seems highly improbable.[27]

Prof. A. Frumkin (*Moscow*) (*communicated*): The influence of the solvent on the overvoltage deserves the attention of investigators and its study can help us to elucidate the mechanism of electrochemical reactions. A theoretical interpretation is, however, possible only if we are sure that the effects observed really represent the influence of a chemically stable medium on the velocity of the electrochemical reaction and that the steady state of the electrode surface is the same in the presence of the different solvents. These conditions are rather difficult to realise in non-aqueous solvents. In the case of the lead electrode the overvoltage values given for the aqueous solution in Bockris's paper, viz. *ca.* 0·85 v. with a c.d. = 10^{-3} certainly do not represent the overvoltage on a clean unoxidised lead surface. On prolonged cathodic polarisation of a lead electrode one obtains stable and much higher overvoltage values; the correct value corresponding to this c.d. is at least equal to 1·17 and probably even by a few centivolts higher.[28] Under these conditions it appears premature to discuss the theoretical significance of the results reported in the paper of Bockris. At any rate, an overvoltage difference of *ca.* 0·7 v. between 50 and 100 % CH_3OH would hardly be accounted for on the basis of any overvoltage theory.

Dr. G. E. Coates (*Bristol*) said: Frumkin [29] has criticised some of Hickling's values for overvoltage at high c.d.'s on the grounds of uncertainty in the extrapolation to zero time of interruption of the polarising current. In view of the bearing of polarisation maxima on the theories of overvoltage I should like to refer to some of the results obtained by Miss P. M. Bryant and myself for the polarisation of platinised platinum electrodes in 0·02 N. HCl, where the polarisation decay graph was in some experiments quite flat up to 1/100th sec. after interrupting the polarising current. In such experiments we feel there is no doubt about the extrapolation, and the existence of maxima in the corresponding polarisation-c.d. curves.

Our experiments have been extended to include cathodes of Cu, Ag,

[24] *Proc. Roy. Soc. A*, 1928, **120**, 59.
[25] Gurney, *Proc. Roy. Soc. A*, 1931, **134**, 137; Eyring, Laidler and Glasstone, *J. Chem. Physics*, 1939, **7**, 1053.
[26] Harned and Fleischer, *J. Amer. Chem. Soc.*, 1925, **47**, 82.
[27] Hickling and Salt, *Trans. Faraday Soc.*, 1941, **37**, 224.
[28] Kabanov and Jofa, *Acta Physicochim.*, 1939, **10**, 617.
[29] Frumkin, *Acta Physicochim.*, 1943, **18**, 23.

Au, Sn, Pb, Ni, W, Pd and Hg, in 0·02 N. HCl; with all these a maximum polarisation is observed or, in some instances, the polarisation becomes almost independent of c.d. These results will be reported more fully in a later communication.

Dr. J. Weiss (*Newcastle*) said: I should like to emphasise that in my paper no special assumption is made as to the nature of the time-determining process. From the above reactions it follows directly that for the stationary state the discharge process must be time-determining (if it precedes the recombination), or is identical with the recombination process as in the case of reaction (2′). It is of considerable importance also to note that reactions (2) or (2′) should more aptly be regarded as *proton transfer* reactions, i.e. transfer of a proton from the hydrated state to the (negatively charged) metal surface. Apart from the *limiting* b and α values given in the paper all the intermediate values can be obtained by a more elaborate treatment of the stationary state equations.

If, on the other hand, one assumes that the reverse reaction of the discharge process (2) also takes place, then the recombination of the H-atoms becomes the time determining process. It is clear, however, that this state of affairs can arise only under conditions of very low over-voltage.

Gurney's original theory is not wrong in principle but it is incomplete as it neglects a number of important features such as the formation of *adsorbed* hydrogen atoms. This is of decisive importance as the formation of *free* H atoms could require a prohibitively large activation energy. For this reason also only ions in the immediate vicinity of the electrode surface can be discharged. Thus the discharge theory should be regarded as a proton transfer from the hydrated ion to the metal surface. It is clear also that under certain conditions the adsorption energy of H atoms largely determines the value of the constant a in the Tafel equation and thus the parallelism with the rate of recombination of H atoms (which depends likewise on the adsorption energy) can be understood.[30] On the other hand the work function of the clean metal as determined by photoelectric or thermionic experiments does not enter as such, because in any case only the *difference* between the work function and the energy of the surface electronic levels plays a part.

An indication of the magnitude of the modified work function can be obtained from some experiments of Suhrmann and Csesch [31] who demonstrated a considerable decrease of the work function with increasing adsorption energy of hydrogen atoms.

No special assumption is made or is necessary with regard to the adsorption of the H_3O^+ ions. However, only the H_3O^+ on or *very* near to the surface of the electrode can be neutralised for the reasons discussed previously.

Dr. J. N. Agar (*Cambridge*) said: In reply to Dr. Hickling, an illustration of the useful information that may be derived from energies of activation is given in my paper; the experimental value of the energy of activation for hydrogen deposition on mercury at the reversible potential in acid solutions is 18 kcal., and this seems to rule out the possibility of formation of free atomic hydrogen, which must involve energies of the order of 50 kcal. The experimental (apparent) energies of activation are, of course, subject to a number of uncertainties, but it is difficult to see how these can amount to 30 or more kcal.

In calculating energies of activation from the temperature coefficient of overpotential it is convenient to introduce the Tafel factor α, but it is not necessary to assume that α is a constant. The important quantity is $\left(\frac{\partial \ln i}{\partial V}\right)_T$ and the value of this quantity (or of the closely related quantity

[30] cf. Volmer, *Physik. Z. Sowiet Union*, 1933, 4, 358.
[31] *Z. physik. Chem. B*, 1934, 25, 215.

α) can be found experimentally at any c.d. and temperature, irrespective of whether the $V - \log i$ curve is linear or not.

The electrode capacity of 20 μF./cm.^{2}, found by Bowden and Grew, is uncertain to approximately ± 2 μF./cm.^{2}, but, in view of the fact that values in the same range have now been found by a number of different methods, it seems unlikely that the true value can differ much from 20 μF./cm.^{2} at the potentials in question. The capacity is, of course, somewhat dependent on the potential, as is shown by Frumkin's work.[32]

In reply to Dr. Butler, as far as I am aware, the only values of energies of activation published since the available data were tabulated in 1938 [33] are those due to Stout.[34, 35] The technique described by Stout shows how reliable results may be obtained.

I think it is important to emphasise the distinction between (i) the step that determines the rate (or overpotential) of an electrode reaction, (ii) the mechanism of the reaction as a whole, and (iii) the process responsible for isotopic separation. For example, if the discharge of hydrogen ions is the rate-determining step in the evolution of hydrogen, overpotential measurements are unlikely to give much useful information about the subsequent course of the reaction. Similarly, measurements of the capacity of mercury cathodes show that the amount of adsorbed hydrogen present is small *if the transition from ion to adsorbed atom is reversible;* this conclusion does not follow if the transition is highly irreversible. In the latter case the amount of adsorbed hydrogen may have little influence on the charging curves or on the steady overpotential, unless certain secondary effects become important, e.g. blocking of a large fraction of the available reaction sites by previously deposited hydrogen.

The possible difference between the steps responsible for overpotential and for isotopic separation may be seen by considering Horiuti's "electrochemical" mechanism:

$$(a)\ H_3O^+ + Me— + e \rightarrow H_2O + H—Me$$

followed by

$$(b)\ H_3O^+ + H—Me + e \rightarrow H_2O + H_2 + Me—.$$

Stage (*a*) may determine the rate and overpotential, but the separation coefficient is determined by (*a*) and (*b*) jointly. On the other hand, if formation of molecules takes place by the "catalytic" or "Tafel" mechanism:

$$(c)\ 2\ H—Me \rightarrow H_2 + 2\,Me—$$

the isotopic composition of the gas evolved must be the same as that of the atoms deposited.

The occurrence of maxima in $V - \log i$ curves has been mentioned in this discussion. I cannot see how these *maxima* can be explained by any simple theory of overpotential—either ion-discharge or atom-recombination—although it is, of course, easy enough to explain *non-linear* $V - \log i$ curves in terms of these theories. It appears more probable that the maxima are really due to some additional effect, e.g. changes in the electrode surface or deposition of low-overpotential impurities at the more negative potentials.

Prof. A. R. Ubbelohde (*Belfast*) said: It is interesting to note that we have an alternative method of investigation the conditions controlling the reaction, $H_2 \rightleftharpoons 2H$ at the surface of the palladium.

Various lines of evidence indicate that, within the lattice, hydrogen is definitely present in the atomic form and in fact a proportion at least of the atoms are dissociated into protons and electrons.[36] Consequently

[32] Proskurnin and Frumkin, *Trans. Faraday Soc.*, 1935, 31, 110.
[33] Bowden and Agar, *Ann. Reports*, 1938, 35, 90.
[34] Stout, *Trans. Faraday Soc.*, 1945, 41, 64.
[35] Stout, *ibid.*, 2nd paper, *this vol.*
[36] Cf. Ubbelohde, *Trans. Faraday Soc.*, 1932, 28, 275; *Proc. Roy. Soc. A*, 1937, 159, 295, where references are given.

when metallic palladium is exposed to molecular hydrogen it cannot enter the lattice faster than the above reaction can produce hydrogen atoms. It has been shown that traces of oxygen poison the surface of the metal for this reaction [37] and that the poisoning is only slowly removed by hydrogen at ordinary temperatures. So far as this poisoning of the reaction, $H_2 \rightleftharpoons 2H$, applies generally at metal surfaces it suggests that considerable caution is required in interpreting *slow* changes of overpotential at electrodes which have had access to the atmospheric oxygen, and may not have been fully reduced before measurements begin.

Prof. A. Frumkin (*Moscow*) (*communicated*): The behaviour of palladium electrodes has been discussed in a paper by Frumkin and Aladjalova[38] which apparently has remained unknown to Stout. Our results differ in many respects from those obtained by him. The conclusions concerning the hydrogen overvoltage on a palladium electrode are quoted in the paper by Frumkin in this Discussion.

For an unpolarised electrode the potential becomes independent of the hydrogen content, when the ratio $r = \dfrac{\text{Atoms H}}{\text{Atoms Pt}}$ drops below a certain value (at room temperature *ca.* 0·6). This is in agreement with the well-known thermodynamic properties of the Pd—H system, as lower values of r fall in the two-phase region and the potential is independent of the relative proportion of the α- and β-phases. On further decrease of r the independence ceases with the disappearance of the β-phase. Earlier data of Nylen [39] agree with these conclusions. I suppose therefore that in the experiments, the results of which are given in Fig. 5 and 6 of Stout's paper, conditions of internal equilibrium have not been realised. If r exceeds 0·6 (homogeneous β-phase), there is under equilibrium conditions a linear relation between potential and hydrogen content. These systems, whose electrochemical properties will be discussed in more detail in a forthcoming paper by Frumkin and Fedorova, are perfectly stable, but of course their equilibrium pressure may exceed one atmosphere at room temperature.

Dr. D. D. Eley (*Bristol*) said: Dr. Bockris gives evidence that a metal with a high work function has a low hydrogen overvoltage. Nevertheless, one must be careful in supposing that the electron from the chemisorbed hydrogen goes into the metal levels in the simple fashion established for highly electropositive elements like Cs. If this were so, the hydrogen end of the dipole would be positive, i.e. $M^- — H^+$, where M is a surface metal atom. The best-established case is probably that of hydrogen on tungsten, due to Bosworth [40] and confirmed by other workers in Rideal's laboratory. Here the bond is largely homopolar, there being a relatively weak dipole $W^+ — H^-$, of moment about 0·4 d., *the hydrogen being negative.*

Dr. Weiss has mentioned the photoelectric work function data of Suhrmann and Csesch.[41] Their data give hydrogen as positive on Pt, Au, Ag, neutral on Tl and negative on Al. For example, they give the work functions on Pt, 6·35 v.; Pt—H, 4·11 v. However, the accepted value for clean platinum is now 5·4 v., and so it is unlikely that the authors' platinum surface was clean. It may be remarked that, except in the case of tungsten, where the surface oxide evaporates well below the melting-point, the greatest difficulty attends the removal of surface oxides from metals, and the surface that results on heating such oxides in hydrogen is often a matter for conjecture.

I have attempted to calculate whether in the case of a surface atom of tungsten the completely ionic states W^-H^+ or W^+H^- are the most

[37] Ubbelohde and Egerton, *Trans. Faraday Soc.*, 1932, **28**, 286.
[38] *Acta Physicochim.*, 1944, **19**, 1.
[39] *Z. Elektrochem.*, 1937, **43**, 915.
[40] Bosworth, *Proc. Camb. Phil. Soc.*, 1937, **33**, 394.
[41] Suhrmann and Csesch, *Z. physik. Chem. B*, 1935, **28**, 215.

stable. The difference in energy of the two states is within the uncertainty which arises from the uncertainty in the length of the W—H bond involved.

Prof. Ubbelohde has raised the question of oxide layers on the electrodes leading to ageing phenomena. The initial presence of oxide layers on metal electrodes is a certainty in *many* cases. How far these layers are reducible by discharging hydrogen is not clear. A further process has been noticed by Roberts.[42] The monatomic layer of oxygen on tungsten in the presence of hydrogen slowly disappears, presumably by diffusion into the metals. Surface oxygen on nickel also slowly diffuses into the interior.[43]

It is again very likely that, however carefully the electrode be freed from oxygen *in vacuo*, on immersion in water it will immediately be covered with a monatomic film of oxygen by

$$M + H_2O \rightarrow M = O + H_2.$$

For tungsten, such a reaction is probably exothermic to the extent of 6 kcal.[44]

If a monatomic film of oxygen exists on a working electrode it may be expected to play an important part in the structure of the double layer, because of its high resistance. There would seem to be a considerable field for investigation of the effect of surface oxygen on hydrogen overvoltage.

Dr. J. Weiss (*Newcastle*) (*communicated*): The neutralisation of oxonium ions at some considerable distance from the electrode with the subsequent formation of free H atoms is energetically impossible. It was shown already by Eyring and Topley that for such a process the activation energy would be prohibitively large.

Dr. J. N. Agar (*Cambridge*) (*communicated*): Frumkin's discussion[45] of the interrupter method[46] of measuring overpotentials indicates that the *apparent* overpotential (actually the overpotential at some constant short interval after interruption of the current) should tend to a limiting value at high c.d.'s. It is worth noting that Frumkin calculates the rate of decay of overpotential by assuming that the electrode behaves as condenser of constant capacity; a different conclusion might be reached if the decay of overpotential follows a different law, e.g. if there are "arrests" in the decay curve. This may explain the fact, mentioned by Hickling, that the interrupter method does give linear V-log i curves for several metals. Bagotzky's results, quoted by Frumkin, constitute very strong evidence in favour of the slow discharge mechanism of hydrogen overpotential on mercury. The earlier results of Levina and Sarinsky, using $LaCl_3$, were not quite so convincing, since it might have been argued that the high field close to a trivalent ion could influence the rate of reaction between adsorbed hydrogen atoms, which no doubt have a dipole moment, to the extent observed. Such an explanation now seems to be out of the question.

The importance of slow changes in overpotential (at constant c.d.) has rightly been emphasised in this discussion. These changes undoubtedly occur on most electrodes other than mercury, and Bockris, and Hickling and his collaborators have shown that reproducible results can be obtained by measuring the overpotential when the final steady value has been attained, which may require periods of the order of an hour. None of the present theories of overpotential can explain such slow changes, except possibly in the case of very small c.d.'s. Unless these theories are

42 Roberts, *Proc. Roy. Soc., A*, 1935, **152**, 445.
43 Beeck, Smith and Wheeler, *ibid.*, 1940, **177**, 62.
44 Eley and Rideal, *ibid.*, 1941, **178**, 429.
45 Frumkin, *Acta Physicochim.*, 1943, **18**, 23.
46 Hickling, *Trans. Faraday Soc.*, 1937, **33**, 1540.

to be rejected entirely, one must conclude that the observed overpotentials are considerably affected by various subsidiary factors capable of giving rise to slow changes, such as alterations in the electrode surface (e.g. deposition of impurities, formation of oxides at anodes and disruption of the surface layers of cathodes), or, possibly, solution of hydrogen in cathodes. There is also evidence [47] that adsorption of capillary-active ions may be rather a slow process.

If this explanation of slow changes is correct, it would seem that information about the electrode reaction proper can best be obtained by measuring overpotentials as rapidly as possible, e.g. by oscillographic or A.C. methods, so as to minimise the alterations of the electrode surface.

Dr. P. Gross (*Slough*) (*communicated*): It would appear from Prof. Wynne Jones' Introduction as if the electrolytic isotope separation can be easily understood if the ion discharge is the rate-determining step, whereas it would be very much more difficult to explain it by assuming that equilibrium is established between hydrogen atoms at the electrode and the hydrogen in the solution. It may be pointed out that, adopting this latter presupposition and with reasonable assumptions for the rates of recombination, a separation coefficient of the right order results almost automatically.[48] Furthermore, even if different assumptions are made concerning the rates of recombination, we are still led, on this view, to predict an effective separation of the isotopes.[49] Experiments by Farkas at palladium electrodes gave results in substantial agreement with this mechanism, the experimental values for the decisive constants of the theory agreeing well with the calculated ones. It appears, therefore, that for palladium as electrode material, at any rate, the isotope separation cannot be taken as evidence in favour of a slow discharge process.

Sir Charles Goodeve (*London*) said: I should like to raise two points. I feel it would have been profitable if more had been said at this discussion about experimental technique. This subject of overvoltage has been made unnecessarily complicated in the past by the variety of techniques used and also by insufficient care on the part of some experimenters. The value of the over voltage found depends, for example, on whether one uses the commutator technique or the direct method, most people considering that the former method gave a value too low and the latter method one too high. Modern electronic techniques, however, permit a measurement of the back E.M.F. at a very short time interval after the current has stopped and with a very low external resistance. This whole question is examined in one paper, that by Ferguson, where it is shown that only at very low c.d.'s is the value of overvoltage obtained by the direct method practically the same as that by the commutator method.

I feel it desirable that we should still look on ordinary overvoltage as being made up of two parts, a back E.M.F. part and a transfer resistance part, and I believe a distinction between these two parts would go a long way towards resolving the dispute between the two theories.

The improvement in experimental technique and reproducibility brings the question of c.d. into more prominence. I would point out, however, that very few experimenters take precautions to ensure that there is uniform c.d. over their electrodes. As is well known, the current from the end of a wire or from the edges of a plate can be many times—even up to 100 times—that on the flat surface. The prevention of this for plates is rather difficult but with a rod or wire you can get almost perfect uniformity by putting a glass bead on the end.

My second point concerns the nature of the metal. There seems still a tendency to consider that the surface of a metal looks to a hydrogen

[47] Frumkin, *Acta Physicochim.*, 1943, 18, 23.
[48] Halpern and Gross, *J. Chem. Physics*, 1935, 3, 452.
[49] Farkas, *Trans. Faraday Soc.*, 1937, 32, 553.

atom rather like it does to us. Although most contributors to this discussion are aware of our modern views on the electrical and wave-mechanical aspects of metals, they seem to pay less attention to the more simple geometrical and crystallographical aspects. We now know that the interstices between the atoms in a metal are quite substantial and certainly large enough to allow the proton to go through with considerable ease. It may have a little more difficulty going through with its electron as a hydrogen atom, but at all events the surface has some resemblance to that of a sponge as far as hydrogen is concerned. The solubility of hydrogen in metals at normal temperature and pressure is admittedly low—it is about 10^{-7} atoms per metal atom in iron—but this is only because hydrogen prefers the lower energy and freer state, that of hydrogen gas. It is well known that if we make iron cathodic, such as in electrolytic pickling, hydrogen goes into the iron vastly in excess of the concentration corresponding to equilibrium with hydrogen gas at one atmosphere. This must on thermodynamic grounds produce a back E.M.F. overvoltage. One might attribute this to a slow combination of hydrogen atoms. My main point here, however, is that we should first attribute it to a local increase of *concentration* of hydrogen in the metal near the surface and not peculiarly as an adsorbed layer.

Dr. A. Hickling (*Liverpool*) said: The President has suggested that the two opposing views of hydrogen overvoltage might be reconciled by supposing that the combination of hydrogen atoms is the rate-determining step on low overvoltage cathodes, while the discharge of the hydrogen ion is the rate-determining step on high overvoltage cathodes. While, of course, there is no *a priori* reason why this should not be so, it appears to me that this dual view meets a fundamental difficulty, and furthermore does not aid greatly in the interpretation of experimental observations. Bonhoeffer has shown by direct experiment that the combination of hydrogen atoms on high overvoltage metals such as mercury and lead occurs much more slowly than on the low overvoltage metals. If then we are to accept the combination of hydrogen atoms as the rate-determining stage on the low overvoltage metals, is it not even more likely that it will be the rate-determining stage on the high overvoltage ones? Also, the slow-discharge views have not, in my opinion, provided any plausible interpretation of the great variety of overvoltage phenomena which have been investigated. For example, we have the variation of overvoltage with time, the influence of catalytic poisons, the ready diffusion of cathodic hydrogen through metals, the electrolytic reduction of organic compounds and its dependence upon the overvoltage of the cathode material. All these phenomena meet with a ready explanation on the atomic hydrogen theory, and I am not convinced therefore that the adoption of the dual view would represent any real advance.

Dr. J. O'M. Bockris (*London*) (*communicated*): The overvoltage of 0·85 v. referred to by Prof. Frumkin was obtained on Pb of 99·993 % purity with a reproducibility of about ± 0·01 v. It represents the overvoltage at a steady state reached after some 2 hr.'s polarisation. The higher results of Kabanov and Jofa [50] were obtained on Pb prepared by cutting with a steel knife. No evidence is recorded in this paper to counteract the conclusion that the pretreatment described would introduce contamination of the surface. A solvent effect of 0·7 v. is exceptionally large. A more typical result [51] is that at a dropping Hg cathode, at which the overpotential is 0·16 v. lower in N. methanolic HCl than in the corresponding aqueous solution.

With reference to Hickling's comment on Grahame's value of 16 μF./sq. cm. for the double-layer capacity at a Hg-solution interface, it seems necessary to point out that the use of wax at some glass-rubber joints in

[50] *Acta Physicochim.*, 1939, **10**, 617.
[51] Bockris and Parsons (in press).

this author's apparatus tends to detract from the weight of his lower result.

Dr. Eley concludes from evidence on chemisorbed hydrogen on clean metals *in vacuo* that mechanisms involving recombination of loosely chemisorbed hydrogen atoms are improbable. Must one not be a little cautious in applying evidence of this kind to conclusions concerned with a working cathode in solution ? It seems relevant to point out that the reaction-rate treatment of this mechanism by Horiuti and Okomoto [52] enables a quantitative agreement with several experimental results on Ni at low c.d.'s to be obtained.

With reference to Butler's remarks concerning Eyring, Glasstone and Laidler's theory,[53] it may be interesting to note that calculation [8] of ΔH from the theory by assuming ΔS to be of the order of that of the reaction $2H_2O \rightarrow H_3O^+ + OH^-$ (as suggested by the authors) yields values which are somewhat greater than those experimentally observed.

The most fundamental result of Frumkin and Aladjalowa's [54] work on hydrogen overvoltage at Pd cathodes seems to me to be the establishment under rigorous experimental conditions of the transfer of overvoltage by diffusion of atomic hydrogen to the non-polarised side of a thin Pd film. This would seem almost conclusive evidence for the importance of the catalytic mechanism on this electrode.

Agar's comment that none of the present theories of overvoltage can explain slow changes with time is somewhat surprising. Such an explanation is surely an important contribution from most slow combination mechanisms. Frumkin and his collaborators,[50, 54, 55] have treated this slow time-variation in recent work. A decision as to what is a primary and what is a secondary effect in setting up the final overvoltage at a metal must usually be somewhat arbitrary.

III DEPOSITION OF METALS.

Introduction.

By A. W. Hothersall.*

In Germany in the early years of this century and somewhat later in Great Britain and U.S.A., the technicians of the Electrochemical industries attempted to apply classical electrochemistry to their technical processes. They achieved some success, but deficiencies in knowledge were very apparent. The culmination of this stage was marked by such outstanding publications as Allmand and Ellingham's *Applied Electrochemistry* and Foerster's *Electrochemie Wasseriger Losungen* and by the last General Discussion held by the Faraday Society in 1924.

In this Discussion there were no papers in which the products of electrolysis were examined to find out what information could be obtained about the electrode process by a knowledge of their structure. Attack on the problem by such methods had however begun to be made at about this time and was continued to an increasing degree using X-ray and later, electron diffraction as well as metallurgical methods of examination. Evidence of the value of these methods of approach was given in the General Discussion on the structure of metallic coatings, films and surfaces held by the Faraday Society in 1935. The closer definition of the nature

[52] Horiuti and Okomoto, *Rep. Inst. Phys. Chem. Res., Tokyo*, 1936, **28**, 231.
[53] *J. Chem. Physics*, 1939, **7**, 1053.
[54] *Acta Physicochim.*, 1944, **19**, 1.
[55] Frumkin, *ibid.*, 1943, **18**, 23.
* Armament Res. Dept., Woolwich. Acknowledgement is made to the Chief Scientist, Ministry of Supply, for permission to publish this note.

of metallic deposits thus obtained opened the way for a new attack to be made on the fundamental problems of electrochemistry and the present Discussion may be regarded as a stock-taking of the progress made.

Two of the chief problems to be solved in studying the structure of electro-deposited metals are inter-related. One is to determine the way in which the grains are built up, what determines their size and their orientation and what is the cause of the stress which appears to be present to some degree in nearly all electro-deposited metals. The other is the relation between the structure of the basis metal and the deposit, which is necessary to give a full understanding of the mechanism of adhesion.

Much qualitative information on the structure of certain electro-deposited metals (especially nickel) is already available and has led to the conclusion that the physical properties of electro-deposited metals can be varied over a much wider range than is possible by working, because the grain size can be made so much smaller. It appears that inclusion of foreign atoms or molecules in nickel deposits interferes with the completion of a growing lattice layer so that a new grain starts to grow ; the presence of oxides and other compounds in nickel deposits has been demonstrated. Whilst this mechanism has been qualitatively established for nickel deposits and is probably true for many other deposits, we still have much to learn about the precise mechanism of entry of these foreign atoms or molecules into the growing deposit. Refined methods of studying electrode phenomena such as are described in some papers before us may help to elucidate this problem if the results are properly co-ordinated with a study of the structure of the deposits.

Finch, Wilman and Yang [1] have given us an exhaustive survey of electron diffraction studies of a wide range of electro-deposited metals on a variety of basis metals, some single crystals, some randomly orientated or amorphous. Their results greatly elaborate but generally support the conclusions outlined above and indicate more precisely the mechanism by which the crystal habit of the deposit is determined.

Finch and his colleagues distinguish three stages in the growth of electro-deposits. During the first, the orientating influence of the basis metal is paramount. The second is a transition stage and in the third the deposit assumes a crystal habit which is governed by the conditions of deposition. The duration of the respective stages differs of course according to conditions. This analysis is supported by previous work which showed that, under carefully selected and controlled conditions, it may be possible for the first stage to continue indefinitely.

Certain metals, for example, lead and silver, tend to deposit from their simple salt solutions as isolated single crystals and deliberate additions of interfering substances must be made to the solution if compact deposits are needed. The value of certain types of organic substance (such as protein colloids) is well known in technical practice but their effective control has always presented a difficulty. The molecules or aggregates of the organic substance are commonly supposed to become adsorbed on the growing deposit, hindering outgrowths by providing the densest population of adsorbed molecules on prominent areas. But little is known of the reasons for the superior behaviour of some materials—is it size or shape of molecule, electrical charge, chemical or physical affinity for the metal ? Beck and Lind [2] suggest from their study of a number of additions to lead perchlorate solutions that the size of the molecule is important.

In this connection, it is interesting to note that Randles [3] studying the kinetics of electrode reactions, has devised a method of determining reaction rates which, when applied in preliminary tests to certain metal deposition processes, indicates that colloids slow up a reaction at the cathode surface without affecting the general rate of diffusion. Here

[1] *This vol.*, p. 144. [2] *This vol.*, p. 285. [3] *This vol.*, p. 11.

possibly is a new tool to assist the electrochemist in his study of the complicated reactions at electrodes.

Passing now to electrochemical studies of electrode processes, the problem of metal overpotential has long puzzled the electrochemist. Developments in electronics have enabled refinements to be made in apparatus for studying overpotential and Salt[4] has adapted and applied Hickling's technique to study the decay of overpotential in nickel deposition. Measurements of overpotential at various times from 3×10^{-6} to 7×10^{-3} sec. from cessation of electrolysis were made under various conditions of c.d., solution composition, *p*H and temperature. One of the chief difficulties connected with this method of studying overpotential is the derivation of the true overpotential by extrapolation of the results to zero time of decay; this is accordingly the part of the paper which should receive critical examination. Using statistical analysis, Salt derived an expression which fits his results obtained at moderate c.d.'s (below 10^{-2} amp./sq. cm.) at which for many of his electrolytes, he found the overpotential to vary with c.d. according to the Tafel equation. The cathodic overpotential was found to change with *p*H and buffering in a way which suggested the formation of nickel hydroxide at the cathodic face. Salt draws no general conclusions about the cause of overpotential which presumably await further data.

The different ways by which solute can move between the bulk of the liquid and the electrode surface have been examined by Agar[5] using the method of dimensional analysis and the dependence of the thickness of the diffusion layer on the concentration difference has been compared for stirred and unstirred solutions. Hoar and Agar have also analysed the factors affecting throwing power (that is, the ability of the solution to produce a deposit of even thickness on an irregular cathode) using an approach and method similar to that of Gardam in an earlier paper.

Much attention has been given in recent years to studies of the mercury dropping electrode with which the name of Heyrovsky is necessarily linked. Heyrovsky[6] has given us further results which have a general bearing on electrode phenomena. The information obtainable by this technique may be unique because of the lack of affinity between mercury and hydrogen and the elimination of the energy involved in placing the atoms on a solid lattice. Heyrovsky submits an unusual explanation of his results which he interprets to mean that the electrolytic acceptance of more than one electron is not simultaneous but consecutive, and that, in the electro-deposition of certain divalent metals for example, the process proceeds electrochemically only to the monovalent stage; thereafter a non-electrolytic rate-determining change occurs (dismutation), e.g. $2\,Zn^{+} \rightarrow Zn + Zn^{++}$.

The papers considered so far have either dealt with the structure of the deposit or with the electrochemical reactions concerned in its production. It is only by a co-ordination of these two lines of approach that a satisfying understanding of electrode processes is likely to be achieved. Gardam[7] has attempted this task by analysing the chain of changes by which the charged ion passes from the bulk of the solution to its final position in the lattice of the solid deposit. He has concluded that an important source of polarisation in the electro-deposition of a solid metal may arise from the energy absorbed in getting the discharged atoms to their final positions in the growing lattice; the effect on the cathode potential of this part of the process may overshadow purely electrochemical effects. This conclusion of Gardam's suggests that the potential is a result of a complicated series of processes rather than the factor that determines which reaction will occur—a point also raised by Hickling.[8]

Electro-deposition is now widely used by engineers for various purposes, such as to impart wear resistance to working surfaces and to protect

[4] *This vol.*, p. 169. [5] *This vol.*, p. 158. [6] *This vol.*, p. 12.
[7] *This vol.*, p. 182. [8] *This vol.*, p. 236.

metals against the erosive action of hot gases. Such applications increased considerably during the war and their success encouraged the hope that further progress in the knowledge of the control of physical properties and adhesion of electro-deposited metals would reveal still more useful applications. Certain alloy deposits have been found to possess interesting physical properties, indicating new possibilities in the field of protective coatings as well as of engineering. Other developments of considerable interest in decorative electroplating are the processes of anodic brightening of metals and the discovery of the phenomenon of smoothing action by which deposits grow to a smooth surface on a rough cathode. Such developments bring new problems with an important bearing on the fundamental changes occurring in the electrode process and they emphasise the gaps in our basic knowledge of such changes. These problems are similar to those which are the subject of this part of the General Discussion and which, as I have tried to indicate, can only be effectively solved by a combined attack on the physical structure of the deposit and on the electrochemical changes in metal deposition and solution.

CRYSTAL GROWTH AT THE CATHODE.

By G. I. Finch, H. Wilman and L. Yang.

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I. Introduction.

The object of study of crystal growth at the cathode is threefold. Firstly, a clear understanding of the processes involved should reveal the principles which govern the growth of the metal crystals and hence also throw light on the nature of the interatomic forces in the deposit. Secondly, this information may help to clarify some unsettled points of the mechanism of electrodeposition and the associated cathodic phenomena. Finally, apart from the theoretical interest, a knowledge of the nature of bonding at the interface of the deposit and the substrate, and of the factors controlling the mode of growth of the deposit, such as crystal orientation, size and habit, may indicate those conditions of deposition which favour adhesion of the deposit to the substrate and the development of other desirable properties, such as hardness and reflectivity.[1–3, 15]

Many authors have investigated the structure of the cathodic deposits since 1905, using either the microscope,[1, 4–6] or X-rays,[3, 7–13] or electron diffraction.[14–19] Although these three methods are complementary, it is only by electron diffraction that direct information can be obtained

[1] Hothersall, *Trans. Faraday Soc.*, 1935, **31**, 1242.
[2] Wood, *ibid.*, 1248.
[3] Hume-Rothery and Wyllie, *Proc. Roy. Soc. A*, 1943, **181**, 331.
[4] Huntington, *Trans. Faraday Soc.*, 1905, **1**, 324.
[5] Blum and Rawdon, *Trans. Amer. Electrochem. Soc.*, 1923, **44**, 305.
[6] Graham, *ibid.*, 427.
[7] Glocker and Kaupp, *Z. Physik.*, 1924, **24**, 121.
[8] Bozorth, *Physical Rev.*, 1925, **26**, 390.
[9] Frölich and Clark, *Z. Elektrochem.*, 1925, **31**, 655.
[10] Frölich, Clark and Aborn, *Trans. Amer. Electrochem. Soc.*, 1926, **49**, 369.
[11] Wood, *Proc. Physic. Soc.*, 1931, **43**, 138.
[12] Clark, Pish and Weeg, *J. Appl. Physics*, 1944, **15**, 193.
[13] Kersten, *Physics*, 1932, **2**, 274, 276.
[14] Thomson, *Proc. Roy. Soc. A*, 1931, **133**, 1.
[15] Finch and Sun, *Trans. Faraday Soc.*, 1936, **32**, 852.
[16] Finch and Williams, *ibid.*, 1937, **33**, 564.
[17] Quarrell, *Proc. Physic. Soc.*, 1937, **49**, 3.
[18] Thirsk, *Ph.D. Thesis* (Univ. of London, 1939).
[19] Cochrane, *Proc. Physic. Soc.*, 1936, **48**, 723.

about the structure of the very thin initial deposit, or even in some cases of thicker deposits.[16]

II. The Relation between Cathodic and other Types of Crystal Growth.

The characteristic conditions governing crystal growth at the cathode are most clearly understood if we consider the relation between the following three types of crystal growth: (i) deposition in vacuum or low pressure gas (condensation from the vapour phase, or cathodic sputtering, or by thermal decomposition, etc.); (ii) crystallisation from solution; (iii) electrodeposition. In (i), which is the simplest case, the atoms soon after arriving at the substrate with a certain amount of kinetic energy, have mobility determined by the thermal motion of the substrate atoms. This average mobility is thus characteristic of the substrate material and its temperature. In (ii), the conditions are similar to those in (i), except that the mobility of the deposited atoms on the substrate at a given temperature is increased by the impacts of the solvent molecules and that there are further influences on the mobility due to adsorption of the various constituents of the solution. In (iii), the conditions are similar to (ii), but with a further characteristic tendency of increased rate of deposition on the projections of the substrate surface, where the electrostatic field is more intense. These different conditions result in differences of the nature of crystal growth in these three types of deposition.

Deposits in vacuum on amorphous substrates at liquid air temperature [20-22] are in general also amorphous or nearly so in thin layers, because the temperature is so low that the mobility of the deposited atoms on the substrate is small and the aggregation of the atoms into crystalline arrangement is hindered. Deposition at room temperature[20, 21, 23-28] on amorphous substrates in general results in crystalline deposits, owing to the higher mobility of the deposited atoms. If their mobility is high enough, the deposited atoms tend to arrange themselves with the most densely-packed lattice plane parallel to the substrate.[20, 24, 25, 28-30] When, however, the atoms are incident obliquely, then, as the deposit grows thicker, the surface region will tend to consist of crystals having the most densely-packed lattice-plane perpendicular to the incident beam.[31-33] On the other hand, if the substrate surface possesses a regular arrangement of atoms, like the face of a single crystal, then, if the mobility of the deposited atoms is high enough, the first thin layers tend to be arranged in such a manner that the lattice plane, not necessarily the most densely-packed one, is parallel to the substrate plane, and the atomic arrangements in them are similar.[34-39] An exact fit in positions of atoms at the

[20] Hass, *Ann. Physik.*, 1938, **31**, 245.
[21] Gen, Zelmanoff and Schalnikoff, *Physik. Z. Sowiet Union*, 1933, **4**, 825.
[22] Ogawa, *Tohoku Univ. Sci. Rep.*, 1937, **26**, 92.
[23] Thomson, *Proc. Roy. Soc. A*, 1929, **125**, 352.
[24] Kirchner, *Z. Physik.*, 1932, **76**, 576.
[25] Prins, *Nature*, 1933, **131**, 760.
[26] Was, *Physica*, 1939, **6**, 390; Was and Tol, *ibid.*, 1940, **7**, 253.
[27] Germer, *Physic. Rev.*, 1939, **56**, 58.
[28] Krautkrämer, *Ann. Physik.*, 1938, **32**, 537.
[29] Volmer, *Z. Physik.*, 1921, **5**, 31. Volmer and Estermann, *ibid.*, 1921, **7**, 13.
[30] Anderson, *Physic. Rev.*, 1932, **40**, 596.
[31] Burgers and Dippel, *Physica*, 1934, **1**, 549.
[32] Burgers and Ploos van Amstel, *ibid.*, 1936, **3**, 1057.
[33] Beeching, *Phil. Mag.*, 1936, **22**, 938.
[34] Lassen, *Physik. Z.*, 1934, **35**, 172. Lassen and Brück, *Ann. Physik.*, 1935, **22**, 65.
[35] Kirchner and Lassen, *ibid.*, 1935, **24**, 133.
[36] Brück, *ibid.*, 1936, **26**, 233. [37] Rüdiger, *ibid.*, 1937, **30**, 505.
[38] Farnsworth, *Physic. Rev.*, 1933, **43**, 900.
[39] Finch, Quarrell and Wilman, *Trans. Faraday Soc.*, 1935, **31**, 1051.

contact plane of the deposit and the substrate is, in most cases, impossible; for the substrate influence to prevail, the maximum allowable difference between the atomic spacings in parallel directions in the contact plane has been noted to be about 15 %, irrespective of the types of crystal growth. In some cases, the substrate influence has even led to the growth of a pseudomorphic form of the deposit crystals.[13, 19, 40]

In crystallisation from solution, even at room temperature the increased mobility of the deposited atoms due to impacts by solvent molecules usually results in large strongly orientated crystals which form in one-degree orientation on amorphous substrates or in two-degree orientation on single-crystal substrates.[41–46] The orientation of deposits of atomic or molecular lattices on amorphous substrates is again such that the most densely-packed lattice plane is parallel to the substrate, although for ionic lattices the plane of orientation is usually the one with the highest population density and containing equal numbers of positive and negative ions. Preferential adsorption of ions, molecules or colloids on certain crystal faces may affect the habit and orientation of the deposit crystals.[47, 48]

In electrodeposition, the crystal growth is similar to that from solution with respect to the relatively high mobility of the deposited atoms over the substrate even at room temperature. There is, however, a tendency of outward growth on the projections of the substrate surface. If the substrate is amorphous or random polycrystalline, the metal deposit nuclei will also be randomly disposed. As the deposition proceeds, a high mobility of the deposited atoms will tend to cause the development of large crystal faces parallel to the most densely-packed lattice-planes; thus, those nuclei which are orientated with these planes parallel to the substrate will grow laterally more rapidly than those in other orientations and receive a large share of the incident atoms and will thus preponderate in the deposit. On the other hand, outgrowth from the projections tends to cause increased deposition on those crystal nuclei which are orientated with the most densely-packed lattice plane perpendicular to the substrate surface. Adsorption of the various bath constituents on the cathode surface is a third important influence on the structure of electrodeposits. It will reduce the mobility of the deposited atoms as well as the tendency of outward growth from projections and, if the bath conditions are such that adsorption occurs in a more or less static manner (see IV (c)), the adsorbed substances will seriously impede the continuous lattice arrangement of the deposit metal atoms and lead to a random deposition of deposit crystals in spite of any substrate orientating influence.

III. The Factors which control the Cathodic Process of Crystal Growth.

From the above considerations, it will be seen that the process of crystal growth at the cathode is influenced primarily by (*a*) the rate of arrival of the metal ions; (*b*) their mobility on the cathode surface before becoming part of a growing crystal; (*c*) the atomic arrangement in the substrate surface on which the ions are adsorbed and discharged; (*d*) the concentration of the electrostatic field near the projecting parts of the more or less rough cathode surface; (*e*) the presence or absence of other

[40] Finch and Quarrell, *Proc. Roy. Soc. A*, 1933, **141**, 398.
[41] Finch and Whitmore, *Trans. Faraday Soc.*, 1938, **34**, 640.
[42] Frankenheim, *Ann. Physik.*, 1836, **37**, 516.
[43] Buckley, *Z. Krist.*, 1937, **97**, 370.
[44] Seifert, *ibid.*, 1937, **96**, 111; 1938, **99**, 16.
[45] Royer, *Bull. soc. France Miner.*, 1928, **51**, 7.
[46] Bunn, *Proc. Roy. Soc. A*, 1933, **141**, 567.
[47] Gaubert, *Compt. rend.*, 1906, **143**, 936; 1918, **167**, 491; 1925, **180**, 378.
[48] Keenen and France, *J. Amer. Ceram. Soc.*, 1927, **10**, 821.

ions, molecules or colloidal substances which can be adsorbed or co-deposited on the cathode.[49] Of these, (*a*), (*b*) and (*e*) are in turn all determined by the following independent factors: (i) concentration of the various constituents in the electrolyte; (ii) bath temperature; (iii) current density and its distribution over the cathode; (iv) the degree of stirring and convection. Except in (iii) for which only the mean values are available, all these factors are observable; they control the bath properties such as conductivity, *p*H value, viscosity and surface tension of the solution. The states of the various constituents in the electrolyte are, however, far from precisely known. There may be present one or more of the following states: simple cations or anions, either hydrated or not; complex cations or anions, either hydrated or not; undissociated molecules and colloidal substances.

It is difficult to predict quantitatively the effects of the above factors, (i)-(iv), on (*a*), (*b*) and (*e*), though some general relationships may be indicated briefly. Thus, for a given c.d., either a higher bath-temperature, or a high bath-concentration or a more vigorous stirring will increase the rate of arrival of metal ions at the cathode by increasing both the speed of the ions themselves and that of the undissociated molecules diffusing towards the cathode region where the ion concentration tends to be impoverished due to deposition. Conversely, a lower bath-temperature and -concentration may reduce the ion concentration near the cathode to such an extent that deposition of hydrogen and other cations occurs, or metallic hydroxides or basic compounds are precipitated [50] and interfere with the mobility of the metal ions on or near the cathode surface. The adsorption of solvent molecules, foreign ions and colloidal materials will always be present to a certain extent on the cathode, but an increase of bath-temperature will cause these to have a more rapidly varying dynamic nature and hence allow more opportunity of access of the metal ions to the cathode surface and also assist their greater mobility over it. This will tend to promote lateral growth of the deposit crystals and yield larger crystals. Even in absence of adsorbed substances on the cathode surface, the velocities of growth on different crystal faces are in general not equal. The more densely-packed planes possess the least velocity of growth along the plane normal, and they therefore form the predominating boundary planes; but if there happens to be a preferential adsorption of some ions, molecules or colloidal substances on certain crystal planes or edges, then the velocity of growth in the directions perpendicular to these planes will be reduced, and the habit of the deposit crystals will be modified accordingly.

Introducing now (*d*) as well as (*a*), (*b*) and (*e*), we may expect that on a rough cathode the tendency will be for the metal ions to be deposited on the peaks where the electrostatic field is more strongly concentrated, the deposit for ing trees extending towards the anode. This tendency, however, can be suppressed if metal ions are supplied from undissociated molecules or complex ions in the electrolyte, when these have a high concentration and a long enough life to diffuse past these peaks and then become dissociated and discharged over the whole cathode surface. In some cases, the presence of colloidal substances or certain organic addition agents often leads to the formation of smooth deposits. The reason for this is presumably due to the strong adsorption of these substances on the cathode surface, especially on projections, thereby not only limiting the crystal growth to many small nuclei and causing small crystal size of the deposit, but also reducing the tendency of preferential growth on the peaks.

Whereas (*a*), (*b*) and (*e*) are influenced by the conditions of deposition as mentioned above, (*c*) and (*d*) are characteristic of the substrate surface

[49] Hunt, *J. Physic. Chem.*, 1932, 36, 2259.
[50] Macnaughtan, Gardam and Hammond, *Trans. Faraday Soc.*, 1933, 29, 729.

which may be atomically smooth or more or less rough, and may be amorphous, polycrystalline (random or orientated and with various crystal sizes) or a single crystal. Owing to the presence of a regularly-spaced unsaturated field of adsorbing forces on or near the surface, it is to be expected that the atomic or ionic arrangement of the substrate surface will play an important part in the determination of the arrangement of the atoms in the initial thin deposit layers. We have found [15] it is a general rule that good adhesion of the substrate is only obtained when there is a strong orientating substrate influence such as described below, whether the substrate is amorphous, polycrystalline or single crystal.

IV. The Structure of Cathodic Deposits and its Relation to the Structure of the Substrate and the Conditions of Deposition.

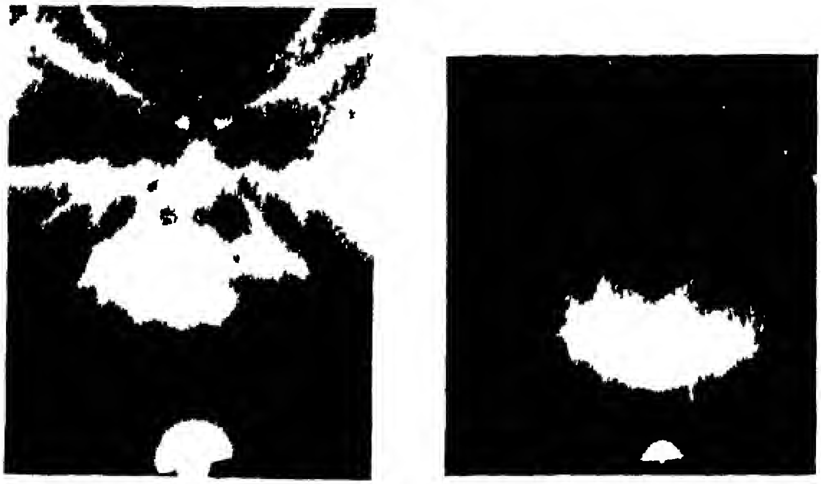
Experimental observations made in this laboratory [15–18, 58] using electron diffraction have shown that, in general, the cathodic process of crystal growth involves three stages: (i) an initial stage during which the structure of the deposit crystals is mainly determined by that of the substrate surface, (ii) a transition stage and (iii) a final stage, only reached in thicker deposits, during which the structure of the deposit crystals is characteristic of the conditions of deposition. We shall describe the growth at each stage in the following paragraphs.

A. The Initial Stage of the Cathodic Process of Crystal Growth.

Three types of substrate surface have been used—single crystal, polycrystalline (random or orientated) and amorphous—and the results will be considered under these headings.

(a) Deposits on Single Crystal Substrates.—The nature of the growth of the first layers of cathodic deposits is most clearly shown in the deposition of a metal from a solution of its simple ions on to a smooth and strain-free surface of a single crystal of the same metal. An electrolytically-polished (100) cube-face of a copper single crystal (about 1 × 1 cm. and polished in a solution containing 63 % by weight of H_3PO_4 and 37 % by weight of H_2O, at 20° c. and 1·0 amp./dm.[2]) was therefore used as the substrate which, after a very light etch in 2 % KCN solution to remove the surface oxide film, gave the electron diffraction patterns shown in Fig. 1 (*a*) and 1 (*b*). From these, we observe: (i) the well-defined Kikuchi lines indicate that the crystal face had a high degree of lattice perfection; (ii) since there are many spots lying on broadened Laue zones, at least part of the surface could not be perfectly flat; (iii) the spots elongated near the shadow edge due to refraction show that much of the surface was extremely, i.e. atomically, smooth though slightly undulating.

Copper was deposited on to this crystal face from a solution containing 200 g. of $CuSO_4 . 5\,H_2O$ and 30 g. of H_2SO_4 per litre of solution at 20° c. and a c.d. of 0·05 amp./dm.[2]. A deposit of average thickness 200 A. gave the electron diffraction pattern (Fig. 2) which shows that the deposit continued closely the structure of the substrate both in crystal orientation and in lattice perfection. The smoothness of the original surface, however, was not maintained. The change from a pattern of elongated spots to one with sharper spots, though with the Kikuchi lines still clearly in evidence, indicates that while the deposit had grown so as to extend the substrate crystal lattice, the new surface was no longer smooth but covered with crystal outgrowths. As the thickness of the deposit was increased to an average value of 500 A., the electron diffraction pattern (Fig. 3) shows the same form as before, except that the Kikuchi lines have become fainter, showing that the surface regions were still rougher and that the pattern was almost wholly due to the transmission



(a) Cube face, beam near cube edge. Spot elongation shows diagonal

(b) Cube face, beam along cube face surface

Fig. 1.—Electrolytically polished Cu crystal

Fig. 2.—Cu deposit 200 A thick on Cu crystal of Fig. 1, beam nearly parallel to cube edge

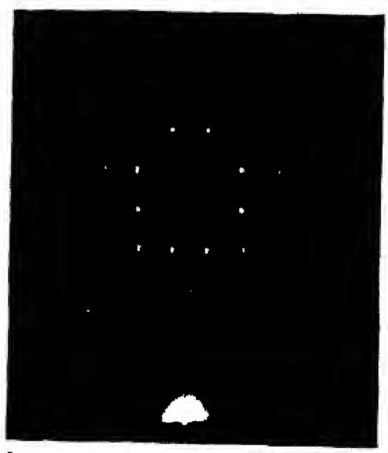


Fig. 3.—Cu deposit 500 A thick on Cu crystal of Fig. 1, beam nearly parallel to cube edge

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(*a*) 11 sec. deposit at 0·1 amp./dm.² and 20° C. Camera length ~ 34 cm. Beam ~ cube edge; octahedral twin spots visible

(*b*) 15 min. deposit at 0·2 amp./dm.² and 20° C. Camera length ~ 34 cm. Beam ~ cube edge; strong Kikuchi lines and few spots show the nearly perfect single crystal structure

FIG. 4.—Au on the approximately cube face of an etched Cu crystal

(*a*) Cu substrate crystal approx. (111) face

(*b*) 10 min. deposit of Au 0·1 amp./dm.² 20° C.

FIG. 5.—Au on the approximately (111) face of an etched Cu crystal; parallel orientation

[*See page* 140

(a) Cu substrate crystal approx. cube face

(b) 2.5 hr. deposit of Ni 0.2 amp./dm.² 50° C

(c) 30 sec. deposit of Ni on etched cube face of a Cu crystal 0.2 amp./dm.² 50° C camera length ~ 34 cm. octahedral twin spots occur strongly besides strongest spots which correspond to Ni lattice parallel to that of the Cu substrate

Fig. 6—Ni on the approximately cube face of unetched Cu crystal parallel orientation

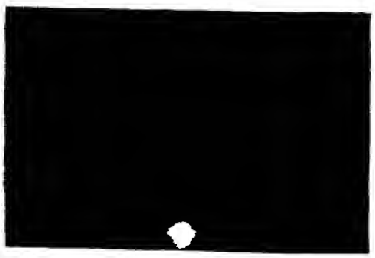
Fig. 7—20 sec. deposit of Cu on etched (111) face of a Cu crystal 0.5 amp./dm.² 50° C strong octahedral twin spots

(a) Deposit thickness 37 000 Å

(b) Deposit thickness 162 000 Å

(c) Deposit thickness 370 000 Å

FIG. 8.—Increase of the degree of orientation with deposit thickness shown by patterns from Ni in (110) orientation characteristic of the bath $NiSO_4.7H_2O$ 30 g./l., H_3BO_3 30 g./l. at 0.25 amp./dm.² and 55° C.



(a) Deposit thickness 2 000 Å: random crystals

(b) Deposit thickness 53 000 Å: (11$\bar{2}$0) orientation and slight (11$\bar{2}$2) also present

FIG. 9.—Zn from cyanide bath: absence of 000*l* rings shows that the deposit crystals have large basal-plane faces, i.e. (0001).

FIG. 10.—Ni from nickel-chloride boric-acid bath; deposit thickness 57 000 Å. The pattern shows both the face-centred-cubic and close-packed-hexagonal forms, in (211) and (10$\bar{1}$0) orientations, respectively.

[*See pages* 152 *and* 156

of the electron beam through these projections. This series of results indicates clearly that, in the initial stage of deposition, the deposit faithfully continues the crystal lattice of the substrate surface but with a gradual increase in the roughness of the surface due to preferential deposition on the projecting parts of the substrate surface.

Deposits of the order of a few thousand angstroms thickness of Cu, Ag, Au, Ni, Co, Cr and Cd on single crystals of Cu, and those of Cu, Ag, Au, Ni and Cr on single crystals of Fe have also been investigated in this laboratory [18] (Table I, and Fig. 4, 5, 6 and 7) and in many cases lattice

TABLE I.—DEPOSITION ON SINGLE-CRYSTAL SUBSTRATES.

Deposit Metal.	Substrate Surface.	Concentration of Bath (g./L).	Temp. °C.	c.d. amp./dm.².	Time of Deposit.	Type of Deposit Crystals.
		Deposition on Cu Single Crystals.				
Ag	(100), (110) and randomly-cut faces	AgCN 32·5	20	0·1	10 sec.	*P*, *T*, some *R* (Fig. 4(*a*))
		KCN 47	20	0·2	45 min.	*P*, *K* (Fig. 4(*b*))
		K_2CO_3 35				
Au	(111)	$NaAuCl_4$ 1·85	20	0·1	10 min.	*P*, *K* (Fig. 5(*b*))
		KCN 17·5				
Cu	(111)	$CuAc_2 . 2H_2O$ 25	60	0·5	20 sec.	*P*, *T*, faint *K* (Fig. 7)
		KCN 35				
		$Na_2SO_3 . H_2O$ 50				
		Na_2CO_3 10				
Cu	(100) polished electrolytically	$CuSO_4 . 5H_2O$ 200	20	0·05	100 sec.	*P*, *K* (Fig. 2)
		H_2SO_4 30	20	0·05	250 sec.	*P*, faint *K* (Fig. 3)
Ni	(100)	$NiSO_4 . 7H_2O$ 60	50	0·2	30 sec.	*P*, *T*, slight *R* (Fig. 6(*c*))
		H_3BO_3 30	50	0·2	2·5 hr.	*P*, faint *K* (Fig. 6(*b*))
Co	(100)	$CoSO_4 . (NH_4)_2 SO_4 . 6H_2O$ 175	20	0·6	20 min.	(110), 1-degree
		NaCl 17				
		H_3BO_3 45	50	0·6	20 min.	*P*, slight *R*
Cr	various	CrO_3 250-500	various conditions			*R* always
		H_2SO_4 2·5-5·0				
Cd	various	CdO 26	20-60	1-3	various	*R* always
		NaCN 75				
		Deposition on Fe Single Crystals.				
Cu	(110)	as above	60	0·5	various	*R* always
Au	(110)	as above	20	0·1	100 sec.	(001) Au//(110) Fe [010] Au//[001] Fe
Ag	(110)	as above	20	0·1-0·2	various	as for Au
Ni	(110)	as above	50	0·2	various	*R* always
Cr	(110)	as above	various conditions			*R* always

P = lattice parallel to substrate crystal lattice.
T = twinning on octahedral planes.
R = randomly disposed crystals.
K = Kikuchi line pattern observed, showing smooth surface and perfect lattice.

continuation similar to the above has been observed. As in other types of deposition, lattice continuation occurred when the lattice spacings in parallel directions in the contact plane of the substrate and the deposit differ by less than about 15 %.

Twinning on octahedral planes was observed in all these relatively thin and strongly orientated deposits on Cu single crystals (including Cu deposited from cyanide bath) but not in Cu deposited on a Cu single crystal from the acid sulphate bath as mentioned above, and in Ag and Au

deposited on Fe single crystals. Such twinning appears to be associated with a considerable difference in lattice spacings of deposit and substrate [51] but may also arise here from the influence of hydrogen evolution. For the cases of Ag and Au on the (110) face of Fe single crystals the orientation is such that there is a close fit in spacings along parallel atom rows of deposit and substrate, and especially in the parallel cube faces which are normal to the substrate surface; correspondingly no twinning was observed, due either to this close fit or the absence of hydrogen evolution or both. This relative orientation was also observed in deposits [15] of Fe on Au and Pd foils which possessed nearly single crystal structure with (100) in the film surface; while parallel growth was found for Cu, Ni and Co on (110) Pt foil, Cu on (100) Pd foil and Co on (100) Au foil but not with Ni on (100) Au foil, whose orientation was the same as that of Fe on (100) Au foil.

Twinning in electrodeposits was also observed by Cochrane [10] and often occurs in thin metal deposits condensed from the vapour phase in vacuum.[34–36] Laue [52] interpreted the patterns as due to the formation of octahedral facets on the deposit surface while the deposit itself had the same orientation as the substrate lattice. Menzer,[53] however, explained the corresponding spots in the patterns as arising from the growing together of the deposit crystals to form a lattice parallel to the substrate lattice although initially their orientations were those of the four octahedral twins relative to that lattice. Goche and Wilman [54] have also pointed out that these extra spots may arise largely from secondary scattering without the need of assuming a large proportion of superlattice formation.

(b) Deposits on Random or Orientated Polycrystalline Substrates.—Finch and Sun [15] found that the first thin layers of electrodeposits growing on random polycrystalline substrates in general also showed random polycrystalline structure. For thin deposits [15] on one-degree orientated substrates prepared by electrodeposition, parallel growth was observed when the deposit and the substrate had nearly the same lattice dimension, but in other cases, such as Cu and Ni on (111) Au, some deposit crystals grew in (100) orientation as well as some in (111) orientation. This (100) orientation does not appear to give a close fitting of the lattice spacings between the deposit metals and the substrate. Much hydrogen was evolved during the deposition and this might have caused some metal hydride formation,[21, 23, 55–57] though in the case of the deposition of Ni on single crystal of Cu the hydrogen evolution had little effect (see Table I), perhaps due to the closeness of their lattice dimensions. In some cases, no parallel lattice orientation occurred, but the orientations gave approximate fitting in position of atoms of the substrate and the deposit along one or more lattice rows in their contact planes, such as (110) Ni and Cu deposits on (111) Fe, (100) Fe on (110) Au, (110) Fe on (111) Au and (110) Sn on (111) Au. In the cases of (110) Ni and Cu on (111) Fe, these orientations were also characteristic of the bath conditions even in very thick deposits.

(c) Deposits on Amorphous Substrates.—Finch and Sun [15] found that deposits of Cu, Au, Ni, α-brass, Pt, Sn, Bi and Zn on mechanically-polished Cu, of Ni and Au on mechanically-polished Ni, and of Au on mechanically-polished Au all had in thin deposits random polycrystalline structure, becoming orientated when they increased in thickness; while Au, Cu,

[51] Wilman, *Proc. Physic. Soc.*, 1940, **52**, 323.
[52] Von Laue, *Ann. Physik.*, 1937, **29**, 211.
[53] Menzer, *Naturwiss.*, 1938, **26**, 385; *Z. Krist.*, 1938, **99**, 378; *ibid.*, 1938, **99**, 410.
[54] Goche and Wilman, *Proc. Physic. Soc.*, 1939, **51**, 625.
[55] Bussem and Gross, *Z. Physik.*, 1933, **86**, 135.
[56] Müller and Bradley, *J. Chem. Soc.*, 1926, 1669.
[57] Hüttig and Brodkorb, *Z. anorg. Chem.*, 1926, **153**, 242.

Ni, Fe and α-brass on an electrodeposited amorphous arsenic layer showed orientations characteristic of the bath conditions even at the initial stage of the deposition. Mechanically-polished metals have relatively smooth though usually slightly undulating amorphous surfaces in which the atoms are arranged in irregular groupings which will act as the equivalent of small crystal nuclei adsorbing strongly the atoms of the first layers of the deposit. The random disposition of these atomic groups will therefore lead to random polycrystalline structure of the deposits. In the case of arsenic substrates these conditions also apply but its adsorbing force on the deposited atoms must be much weaker than that of the above metals which have higher melting points and surface tension. Both these circumstances will promote the growth of deposits having the orientations determined by the conditions of deposition.

It must be pointed out that, although the crystal orientation of the first thin layers of the deposit depends chiefly upon the nature of the substrate as described above, yet Sun [58] found that within $\pm 0{\cdot}2\ \%$ the lattice dimensions of Pt on Ag, Au and Zn on Cu, Ni and Cu on Au, Cr on Au on Cu, Fe on Ni, Cu and Ni on Pt and Fe and Cu on Pd all had normal values, all these substrates being polycrystalline, either random or orientated. The dissolution of the first thin layers of deposit in amorphous mechanically-polished metal surfaces, however, has been observed.[15] Thus, zinc only gave its crystalline type of electron diffraction pattern when deposited for 3 min. or more on a mechanically-polished copper surface, but did so after only 30 sec. deposition under the same conditions on a crystalline copper surface. The crystal size of Cr deposited on Cu and Ni was found [58] to be smaller than that deposited under the same conditions on Fe, Sn and Bi, although the nature of the substrate is, of course, not the only controlling factor.

B. The Transition Stage.

So far we have considered the structure of thin electrodeposits. The orientating influence intiatied by the substrate becomes gradually less as the thickness of the deposit increases, because as we have mentioned in the introduction, various detrimental effects associated with the deposition of metal ions (such as the adsorption or co-deposition of hydrogen and foreign ions and the inclusion of metal hydroxides and colloidal substances) may disturb the regular lattice formation of the deposit crystals. Also the c.d. used and the temperature of the bath may favour the development of another orientation which is not the same one as that initiated by the substrate surface.

If the substrate is a single crystal and the rate of deposition is slow, the orientation initiated by the substrate surface may be followed to a thickness of the order of 40,000 A. or even more.[18, 19] On a polycrystalline substrate composed of small crystals (a few hundred A. in diameter) in one-degree of orientation, the initial orientation stage extends to about 1,000-2,000 A.[16] and is followed by a random transition stage before the development of the orientation characteristic of the bath conditions appears at a much greater thickness.

On random polycrystalline substrates, thin deposits consist of crystals in orientations corresponding to those of the individual substrate crystals and therefore they are randomly disposed, but as the thickness increases, the bath conditions promote the rapid growth of those crystals having certain definite orientations characteristic of these conditions (see below). For example, Finch and Williams [16] found that Ni deposited on random polycrystalline Cu (a few hundred A. in diameter) developed such bath orientation even at a thickness of 2,000 A., while on macroscopic crystalline

[58] Sun, *Ph.D. Thesis* (Univ. of London, 1935).

Cu ($\sim$ 0·01 mm. in diameter), the Ni continued both the crystal size and orientation of the individual Cu crystals up to 5,000 A.

C. The Final Stage of the Crystal Growth at the Cathode.

As we have just mentioned, the random transition layer does not last for more than a few thousand A. if the bath conditions favour the development of a certain orientation. After this stage, the nature of the growth is solely determined by the conditions of deposition. The orientations developed in thicker deposits have been described by Finch and Sun [15] for many metals deposited at one particular bath concentration and c.d. in each case. The orientations found were independent of the nature of the substrate. Finch and Williams [16] also explored the connection between the bath concentration and c.d. and the thickness of Ni deposits (up to 30,000 A.) on Cu.

We have further investigated the relation between bath conditions and the corresponding orientations developed for Au, Ag, Cu, Fe, Ni, Co, Pb, Zn, Cd, Sn, Bi and Sb on the smooth amorphous surface of mechanically polished brass. The characteristic orientations were studied mainly over a range of thickness of 20,000 to 50,000 A. and in a few cases, up to 100,000 A. or more. Under constant bath conditions, the type of orientation developed was found to be independent of the thickness of the deposit in all cases, but the orientation became more and more pronounced, as shown by Fig. 8, which reproduces patterns obtained from Ni deposited from a nickel-sulphate boric-acid bath at 55° C. and 0·25 amp./dm.^{2}, but of different thicknesses.

The results for all the metals studied, under different bath conditions, fall into four groups:

(*a*) amorphous deposits,
(*b*) the deposit crystals are randomly disposed;
(*c*) the deposit is orientated with a less densely-packed lattice plane parallel to the substrate surface;

  (1) the plane of orientation is the lattice plane which is perpendicular to the most densely-packed atom rows in the most densely-packed lattice plane which is normal to the surface of the substrate;

  (2) the plane of orientation is different from that in (1).

(*d*) the deposit is orientated with the most densely-packed lattice plane parallel to the substrate surface.

The bath conditions associated with each of these types of structure can be interpreted easily from the consideration of (i) the tendency of lateral growth when there is high mobility of the deposited atoms on the substrate; (ii) the tendency of outward growth from the projections of the substrate surface; (iii) the presence of adsorbed substances, especially hydrogen ions or atoms, on the cathode surface, and other factors which may influence the mobility of the deposited atoms, such as the evolution of hydrogen gas.

Although (i) and (ii) have been discussed in the introduction, the way in which the adsorbed hydrogen ions or atoms affect the growth of the deposit crystals needs further explanation. Hydrogen ions are usually more or less adsorbed in a state of dynamic equilibrium on the cathode surface. When the cathode potential exceeds the reversible deposition potential of hydrogen ions in the corresponding solution, however, the hydrogen ions, brought to the cathode surface by the applied electric field, will become more strongly adsorbed. They are not evolved as gas until the cathode potential has attained a more negative value than the sum of the reversible hydrogen deposition potential of the solution and the minimum hydrogen overvoltage of the cathode metal, below which

the adsorbed hydrogen, either in the form of ions or atoms, will be accumulated on the cathode surface. A higher hydrogen overvoltage of the cathode metal corresponds to a greater difficulty of the transformation of these adsorbed hydrogen ions or atoms into hydrogen gas, though the nature of this overpotential is still not clear. If these adsorbed hydrogen ions or atoms can be removed as hydrogen gas, it is evident there will be more free space on the cathode surface, though only transiently, for the growth of the deposit metal crystals. Excessive evolution of hydrogen gas of course hinders the growth of the deposit crystals, but the accumulation of adsorbed hydrogen ions or atoms on the cathode surface in a more static manner is still more detrimental.

The experimental results are set forth under headings indicating the nature of the deposit, as follows :

(*a*) **Amorphous Deposits.**—When the deposited atoms have weak *cohesive forces (soft metals with low surface tension)* and the bath conditions are such that there is an accumulation of adsorbed hydrogen ions or atoms on the cathode, the deposit may be amorphous. Thus, when Sb was deposited from an $SbCl_3$ bath (200 g. $SbCl_3$ and 300 cc. conc. HCl per litre of solution) at 20° C. and 0·65 amp./dm.^{2}, the deposit was amorphous.[15, 13] Although Sb atoms have a relatively high mobility even at room temperature, as shown by the low m.p. of Sb and also by direct observation,[59] their cohesive forces are weak. The evolution of hydrogen which should occur in this strong acidic bath containing a low concentration of Sb^{+++}, was not observed, owing to the hydrogen overvoltage of Sb, the current efficiency being 100 %. The amorphous nature of the deposit was evidently caused by the weak cohesive forces and the accumulation of adsorbed hydrogen ions or atoms on the cathode surface, hindering the lattice formation of the deposited Sb atoms. By increasing the bath temperature and hence decreasing the hydrogen overvoltage as well as increasing the mobility of the deposited Sb atoms, hydrogen was evolved and a deposit of about 40,000 A. thickness at 38° C. from the same bath was crystalline but random ; deposits at 50° C. showed weak (100) orientation and those at 75° C. and 95° C. showed stronger (100) orientation (see Tables II and IV).

Finch and Sun [15] also found that As deposited at 80° C. and 0·6-0·8 amp./dm.^{2} from a solution containing 50 g. As_2O_3, 20 g. $Na_4P_2O_7 . 10H_2O$ and 50 g. KCN per litre was amorphous ; and so also was Se deposited at 20° C. and 1·6 amp./dm.^{2} from a bath containing 280 g. H_2SeO_3, 500 g. H_2F_2 and 195 g. H_2SO_4 per litre of solution. The cohesive forces of these elements are also weak.

(*b*) **Random Deposits.**—Metals of higher cohesive forces (e.g. higher surface tension), such as Sn, Pb, Bi, Zn, Cd, Cu, Ni, Co, Fe, Ag and Au always give crystalline deposits and the deposit crystals are randomly arranged (Table II) under conditions when (i) there is an excessive evolution of hydrogen gas, i.e. the curent efficiency is low ; or (ii) there is an accumulation of adsorbed hydrogen ions or atoms on the cathode surface owing to the high hydrogen overvoltage of the deposited metal. Both of these will reduce the mobility of the deposited metal atoms over the cathode surface as well as the tendency of outward growth of the deposit crystals from the projections of the cathode surface and lead to a random disposition of the deposit crystals.

Of the above metals, deposits of those with comparatively weak cohesive forces, such as Bi, Sb and Sn, are found to be less resistant to the disturbances due to hydrogen evolution on their growth than the harder metal deposits, such as Ni, Au, Fe, etc., which possess stronger cohesive forces. The metals with weaker cohesive force usually show random structure even at a current efficiency of 80 or 90 %, while under approximately the same current efficiency, the deposits of the harder metals

[59] Ruedy, *Physic. Rev.*, 1941, 59, 926.

may be highly orientated (compare Table II and Tables III, IV and V).

The adsorbed hydrogen ions or atoms have more influence on the crystal growth when the deposited metal has a high hydrogen overvoltage, such as Zn. Cd and Pb. Deposition under conditions when the hydrogen atoms or ions are not evolved as gas but accumulated on the cathode surface always leads to random deposit. In some cases, however, by raising the c.d. and giving the cathode potential a more negative value, the evolution of hydrogen begins to occur and the deposit is orientated. For example, Cd deposited from a cyanide bath at 20° C. and 1·25 amp./dm.² (see Table II)

TABLE II.—THICK RANDOM DEPOSITS ON MECHANICALLY POLISHED BRASS.

Metal.	Crystal System	Electrolytic Solution g./l.		Temp. °c.	c.d. amp./dm.².	Current Effic. %.	Deposit Thickness 10³ A.
Au	*F.c.c.*	$AuCl_3$	1·5	20	0·25	40	15-32
		KCN	7·2				
		NaCl	0·4				
Fe	*B.c.c.*	$FeSO_4(NH_4)_2$		25	1·25	70	20-50
		$SO_4 . 6H_2O$	350	80	1·25	70	20-40
		H_2SO_4	2·5				
Sn	*B.c.t.*	$Na_2SnO_3 . 3H_2O$	100	70	0·25	80	30-50
				70	0·05	75	30-50
		NaOH	12·5	70	1·25	73	20-42
Sb	*Rhom.*	$SbCl_3$	200	35	0·05	96	20-40
		HCl	300 cc.	75	2·5	60	30
Bi	*Rhom.*	Bi_2O_3	50	50	0·75	90	20-65
		$HClO_4$	93	50	2·50	82	40-85
Cd*	*H.c.p.*	CdO	32	20	1·25	100	30-56
		KCN	83				
Zn*	*H.c.p.*	$ZnSO_4 . 7H_2O$	100	20	1·25	100	20-41
		H_3BO_3	6	20	2·50	100	20-33
		NaCl	4	60	1·25	100	20-32
Pb*	*F.c.c.*	$Pb(ClO_4)_2$	203	20	0·6	100	18-30
		$HClO_4$	50				
		Gelatine	0·5	55	0·6	100	20-30

F.c.c. = Face-centred cubic. *H.c.p.* = Hexagonal close-packed.
B.c.c. = Body-centred cubic. *R* = Random.
Rhom. = Rhombohedral. *B.c.t.* = Body-centred tetragonal.

* = Hydrogen gas should be evolved under these conditions but suppressed by hydrogen overvoltage.

had random structure, the current efficiency being about 100 %; but if the c.d. was increased to 3·75 amp./dm.², with other conditions unchanged, evolution of hydrogen was observed (current efficiency about 95 %) and the deposited Cd showed weak $(11\bar{2}2)$ orientation (see Table IV).

(c) Deposits Orientated with a less Densely-packed Lattice Plane Parallel to the Substrate.

1. Deposits with the Plane of Orientation Perpendicular to the most Densely-packed Atom Rows in the most Densely-packed Lattice Plane.—This is observed under conditions (i) when there is no accumulation of adsorbed hydrogen ions or atoms on the cathode surface; (ii) when the mobility of the deposited atoms over the cathode surface

is low, due to low bath temperature or the evolution of hydrogen, though not in excessive amount; (iii) the rate of supply of metal ions to the hollows of the cathode surface by diffusion and ionisation is slow, i.e. low bath temperature and low concentration; (iv) a further contributing factor, not always present, is that the metal ions in the solution occur only as simple ions which tend to be drawn to the projections and do not reach the hollows of the cathode surface. Under these conditions, deposition on random amorphous substrates will take place to a greater

TABLE III.—THICK DEPOSITS WITH PLANE OF ORIENTATION PERPENDICULAR TO THE MOST DENSELY-PACKED ATOM ROWS IN THE MOST DENSELY-PACKED LATTICE PLANE.

Metal.	Crystal System.	Electrolytic Solution g./l.		Temp. °C.	c.d. amp/dm.^{2}	Current Eff. %	Deposit Thickness 10^3 A.	Orientation of the Deposit.
Au	*F.c.c.*	$AuCl_3$	10	20	1·25	63	15-45	*W* (110)
		KCN	36					
		NaCl	2					
Ag	*F.c.c.*	AgCN	35	20	3·0	80	26-35	*W* (110)
		KCN	37					
		K_2CO_3	38					
Cu	*F.c.c.*	$CuAc_2 . 2H_2O$	25					
		$Na_2SO_3H_2O$	50	15	0·25	55	30-50	*M* (110)
		Na_2CO_3	10					
		KCN	35	75	1·25	66	24-45	*M* (110)
		$CuSO_4 . 5H_2O$	200	15	0·25	98	25-45	*W* (110)
		H_2SO_4	30	15	1·25	94	20-40	*W* (110)
Ni	*F.c.c.*	$NiSO_4 . 7H_2O$	240	17	0·65	45	20-45	*W* (110)
		H_3BO_3	30	17	1·25	75	20-40	*M* (110)
Co	*F.c.c.* and *H.c.p.*	$CoSO_4(NH_4)_2$						
		$SO_4 . 6H_2O$	200	20	2·50	90	30-52	*W* (110) and
		H_3BO_3	30					*W* $(11\bar{2}0)$
Fe	*B.c.c.*	$FeSO_4(NH_4)_2$						
		$SO_4 . 6H_2O$	350	25	3·75	90	20-37	*M* (111)
		H_2SO_4	2·5					
Bi	*Rhom.*	Bi_2O_3	50	24	0·75	98	28-85	*W* $(1\bar{1}0)$
		$HClO_4$	93					
Zn	*H.c.p.*	$Zn(CN)_2$	48	40	1·25	40	16-53	*M* $(11\bar{2}0)$
		KCN	64					and
		Na_2CO_3	4	70	1·25	81	20-50	*VW* $(11\bar{2}2)$

S = strong; *M* = medium; *W* = weak; *VW* = very weak.

extent on the projecting parts of the surface and the initial randomly-disposed crystal nuclei of the deposit will grow out more rapidly if they have the most densely-packed lattice-planes perpendicular to the substrate. These deposit crystals, now projecting further towards the anode, acquire a larger share of the incident atoms. Although this orientation preponderates in thicker deposits, this may still at first only involve the normal of these most densely-packed lattice-planes being parallel to the substrate, so that the electron-diffraction pattern still consists of rings. The velocities of growth in the different directions of these planes are,

however, not equal, being greatest in directions along the most densely-packed atom rows in these planes. Hence, as the deposition proceeds, those deposit crystals which have these lattice rows normal to the substrate surface will grow most rapidly and tend to preponderate. Therefore, the plane of orientation developed in thicker deposit is the lattice plane which is perpendicular to the most densely-packed atom rows in the most densely-packed lattice plane, the latter being normal to the cathode surface. For the close-packed hexagonal, face-centred cubic, body-centred cubic and rhombohedral metals, the lattice planes which meet the above requirements are (11$\bar{2}$0), (110), (111) and (1$\bar{1}$0) respectively. Table III shows the close agreement between the experimental observations and the above considerations.

The case of Zn affords another excellent illustration. Zn deposited from a cyanide bath at 40°c. and 1·25 amp./dm.^{2} and to a thickness of about 2,000 A. gave an electron diffraction pattern as shown in Fig. 9 (*a*). The 000*l* rings corresponding to the basal planes were missing and the 10$\bar{1}$2 and 10$\bar{1}$3 rings were diffuse and indistinct. This shows that the

TABLE IV.—THICK DEPOSITS WHOSE PLANE OF ORIENTATION IS A LESS DENSELY PACKED LATTICE PLANE BUT DIFFERENT FROM THOSE IN TABLE III.

Metal.	Crystal System	Electrolytic Solution g./l.		Temp °c	c.d. amp dm^2	Current Eff. %	Deposit Thickness 10^3 A.	Orientation of the Deposit.
	F.c.c.	$NiSO_4 . 7H_2O$	240	55	1·25	80	50-120	*S* (100)
		H_3BO_3	30					
Ni	*F.c.c.* and	$NiCl_2 . 6H_2O$	140	17	0·25	75	31-57	*S* (211) cubic and
	H.c.p.	H_3BO_3	30	17	0·65	80	20-45	*S* (10$\bar{1}$0) Hex.
Cd	*H.c.p.*	CdO	32					
		KCN	88	20	3·75	95	20-50	*W* (11$\bar{2}$2)
Sb	*Rhom.*	$SbCl_3$	300	50	0·65	94	30-42	*VW* (100)
		HCl	300 cc.	75	0·65	92	32-45	*W* (100)
				95	0·65	90	40	*W* (100)

deposit crystals were flat plates parallel to 000*l* and of relatively large extent in these planes, because the *hk*0 rings were sharp. The crystals might be random but it seems probable that the basal planes were perpendicular to the surface, i.e. [0001] parallel to the surface because thicker deposit (53,000 A.) made under the same conditions gave an arced electron diffraction pattern, Fig. 9 (*b*), showing (11$\bar{2}$0) orientation (also very weak (11$\bar{2}$2) orientation) but, as in Fig. 9 (*a*), the 000*l* rings were missing.

2. Deposits with other Types of Orientation.—In some cases, the deposit crystals are orientated with those less densely-packed lattice-planes parallel to the substrate, which do not meet the requirements mentioned in (1) (Table IV). This may be due to some cause which is not clear at present, although the (11$\bar{2}$2) orientation of Cd has also been noted for Cd crystals deposited from the vapour phase in vacuum. For Ni, which has a high tendency to become twinned on the octahedral planes, the situation becomes more complicated. Thus Fig. 10 is an electron diffraction pattern of Ni (deposited from a nickel chloride-boric acid bath; see Table IV) which possesses both the face-centred cubic and the hexagonal close-packed structure due to twinning on the octahedral planes.

(*d*) Deposits Orientated with the most Densely-packed Lattice Planes Parallel to the Substrate.—There will be a tendency for those crystal

nuclei having the most densely-packed lattice-planes parallel to the substrate to grow sideways more rapidly than the others if (i) there is no accumulation of adsorbed hydrogen ions or atoms on the cathode surface; (ii) the bath temperature is high, ensuring high mobility of the deposited atoms over the cathode surface and a high rate of diffusion of metal-containing molecules to the cathode region; (iii) little or no hydrogen evolution occurs during the deposition; (iv) there are present other factors which will suppress the tendency of outward growth, such as the presence of little-dissociated complex ions of the deposited metals in the solution. The lateral expansion of these planes enables them to receive more incident metal ions than the other lattice planes and the deposit crystals will be orientated for the most part with these most densely-packed lattice-planes parallel to the cathode surface. This is illustrated in Table V.

TABLE V.—Thick Deposits Orientated with the most Densely packed Lattice Plane Parallel to the Substrate.

Metal.	Crystal System.	Electrolytic Solution g./L.		Temp. °C.	c.d. amp / dm.²	Curr. Eff. %.	Deposit Thickness 10^3 A.	Orientation of the Deposit.
Au	*F.c.c.*	$AuCl_3$	10	20	0·25	100	15-30	*M* (111)
		KCN	36					
		NaCl	2	50	0·25	100	27-42	*M* (111)
Ag	*F.c.c.*	AgCN	35					
		KCN	37	20	0·1	100	30-40	*M* (111)
		K_2CO_3	38					
Cu	*F.c.c.*	$CuAc_2 . 2H_2O$	25					
		$Na_2SO_3 . H_2O$	50	75	0·25	84	30-50	*M* (111)
		KCN	35					
		Na_2CO_3	10					
Fe	*B.c.c.*	$FeSO_4 . (NH_4)_2$						
		$SO_4 . 6H_2O$	350	80	3·75	90	20-43	*M* (110)
		H_2SO_4	2·5					

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Summary.

The cathodic process of crystal growth, as revealed by electron diffraction and described above, is a process involving three stages and controlled by various factors which fall under two principal headings, the substrate influence and the bath influence. It is their net effect which determines the process of growth at each stage. The adhesion of the deposit is good [15] if the substrate influence in the initial layer is not counteracted by the bath influence. The other properties of thicker deposits are, however, determined by the bath conditions.

Résumé.

Comme le révèle la diffraction des électrons, la croissance d'un cristal à la cathode comporte trois stades et est contrôlée par divers facteurs, qui peuvent être rangés sous deux rubriques principales : l'influence du substrat et celle du bain. C'est leur effet résultant qui détermine le

processus de croissance à chaque étape. L'adhérence du dépôt est bonne, si l'influence du substrat dans la couche initiale n'est pas contrariée par l'influence du bain. Cependant les autres propriétés de dépôts plus épais sont déterminées par le bain.

Zusammenfassung.

Elektronenbeugungsversuche haben gezeigt, dass der Kristallwuchs an der Kathode ein aus drei Stufen bestehender Prozess ist. Die darauf einwirkenden Einflüsse fallen in zwei Hauptgruppen, u.zw. (*a*) durch das Substrat und (*b*) das Bad verursachte. Der Nettoeffekt dieser Einflüsse kontrolliert den Kristallwuchs bei jeder Stufe. Die Haftfestigkeit des abgeschiedenen Metalls ist gut, wenn der Substrateinfluss auf die erste Schicht nicht durch den Einfluss des Bades zunichte gemacht wird. Die anderen Eigenschaften von dickeren Niederschlägen werden aber vom Zustand des Bades bestimmt.

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THE INFLUENCE OF CHANGE OF SIZE IN ELECTROCHEMICAL SYSTEMS.

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There are many practical cases of electrolytic cells of large size. Familiar examples are electroplating, electro-cleaning and electro-winning vats; "stray-current" cells set up between earthed return mains and buried structures; galvanic cells involving ships' propellers and hulls; and the more complex cells that arise when zinc protectors and other forms of cathodic protection are applied to such stray-current and galvanic systems. On the other hand, electrolytic cells of very small size are also of considerable interest. Examples are the cells set up in oxide-film pores in the early stages of corrosion; the similar cells associated with pitting and intergranular corrosion; and the cells set up during the acid attack or the metallographic etching of polyphase alloys.

It is often convenient to study the electrolytic processes of both large- and small-scale systems by experiments of "laboratory" size, using electrode areas ranging from a few mm.^{2} up to about 1 dm.^{2} and cells ranging from a few mm. to a few cm. in linear dimensions. We shall show in this paper that such "model" experiments do not reproduce the conditions of electrode polarisation and current distribution found on the original scale, unless a proper adjustment of electrolytic conductivity is made.

Cells of Different Sizes with the same Electrolyte.

Consider two electrolytic cells, A and B in Fig. 1, that differ only in size, the electrode reactions and electrolyte being the same. The E.M.F. responsible for the flow of current may be due to a difference in the open-circuit potentials of the two electrodes or to an external source. In either case, the total E.M.F. arising in the circuit has to overcome:

(*a*) the resistance of the electrolyte;
(*b*) polarisation at the two electrodes;
(*c*) the (metallic) resistance of the external circuit.

The resistance of the electrodes themselves is assumed to be negligible, so that all points within an electrode are at the same potential. We define the "available voltage," V_a, as that part of the total E.M.F. which is absorbed in overcoming (*a*) and (*b*).

Let E_1 and E_2 be the polarisations at arbitrarily chosen points P and Q on the electrodes 1 and 2 (Fig. 1), and let V_r be the voltage drop in the solution between a point immediately adjacent to P and another point immediately adjacent to Q. The polarisation is defined as the difference between the potential of a working electrode and potential of the same electrode on open circuit; E_1, E_2, V_r and V_a are all taken to be positive without regard to the usual conventions. We thus have

$$E_1 + E_2 + V_r = V_a. \qquad (1)$$

The current density generally varies from point to point of the electrode surface, and in consequence E_1 and E_2 vary according to the position of P and Q. It has been assumed that the electrode itself is equipotential, but the solution in immediate contact with it will usually not be so, owing to the variation of E_1 and E_2; it follows that the current lines in the electrolyte do not in general cut the electrode normally, that is, there is a tangential as well as a normal component of current density at the electrode. The normal component, i_n amp./cm.², determines the number

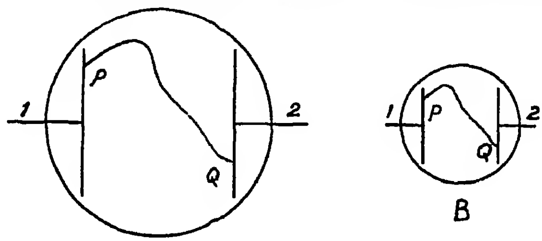

FIG. 1.

of ions crossing the electrode solution interface and the polarisation, and it is this component which is commonly called the "current density" in the discussion of electrode reactions.

If we now consider any line joining P and Q, we have

$$V_r = \frac{1}{\kappa}\int_P^Q i_s \, . \, ds \qquad (2)$$

where κ is the specific conductivity of the electrolyte (assumed to be the same at all points), i_s amp./cm.² is the component of current density in the direction of the line at any point on it, and ds is an element of length measured along the line. If the total length of the line is l cm. we may write $ds = l d\sigma$, where σ denotes position along the line measured as a fraction of its total length. Hence (2) becomes

$$V_r = \frac{l}{\kappa}\int_0^1 i_s \, . \, d\sigma \qquad (3)$$

which, in combination with (1), gives

$$E_1 + E_2 + \frac{l}{\kappa}\int_0^1 i_s \, . \, d\sigma = V_a. \qquad (4)$$

The electrolysis in the two cells may be controlled either by adjusting the "available voltage" or by adjusting the current by external resistances. Two important operating conditions may be considered.

Case (i).—The "available voltage" is the same in both cells. This is

usually the case in corrosion cells, where the total E.M.F. is equal to the difference of the open-circuit potentials of the anodic and cathodic areas, and the resistance of the metallic part of the circuit is negligible.

Case (ii).—The *average* c.d. at the electrodes is the same in both cells, i.e. the total current is proportional to the area of the electrodes. This is the case in electroplating.

If cell B were a "true" model of cell A, the current densities and potentials would in both cases be the same at all corresponding points in the two cells; hence, if we consider geometrically similar lines joining corresponding points, P and Q, on the electrodes, V_r and $\int_0^1 i_s \, . \, d\sigma$ must each be the same in both cells.

Inspection of equation (3) shows that this cannot be true, since the factor l/κ is greater in cell A than in cell B. Hence B cannot be a true model of A.

Very Large and Very Small Cells.

Case (i): V_a Constant.—Since all the terms in (1) or (4) are positive, V_r must always be less than V_a. Hence, when l is made very large, i.e. in a very large cell, i_s must on the average become very small; since no restrictions have been placed on the position or direction of the line considered, this must be true of the current density in general, including the normal component at the electrodes. In consequence, E_1 and E_2 become very small and we have

$$V_r \gg E_1 + E_2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$V_r \sim V_a$$

The polarisation is thus negligible in a very large cell, as indicated by Kasper[1]; the magnitude of the current is controlled by the resistance of the solution and its distribution approaches that which would be observed with unpolarisable electrodes. The current density at any point is then given by an expression of the form

$$i = \left(\frac{C\kappa}{l}\right) V_a \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where C depends only on the position of the point within the cell.

On the other hand, if l is made very small, we ultimately reach a condition in which

$$V_r \ll E_1 + E_2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$E_1 + E_2 \sim V_a$$

The magnitude and distribution of the current are now controlled by the polarisations; if the polarisation curves have the same form at all points on the electrodes, the current density is uniform.

Case (ii): Mean C.D. Constant.—In this case, equation (4) still holds, but V_a is no longer constant; on the other hand, the mean current density on the electrodes does not alter when l is increased, so that E_1 and E_2, and the values of i_s at corresponding points in the two cells, must, in general, remain constant as regards order of magnitude. Both V_r and V_a thus increase with l, and for very large l we have as before

$$V_r \gg E_1 + E_2 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and

$$V_a \sim V_r$$

The distribution of current and potential are approximately the same as for unpolarisable electrodes, and the mean current density is related to V_a by an equation of the same type as (6).

[1] Kasper, *Trans. Electrochem. Soc.*, 1940, 78, 131.

For very small l, we again have

$$V_r < E_1 + E_2 \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

and

$$V_a \sim E_1 + E_2$$

and polarisation is the decisive factor.

The above discussion shows qualitatively that the resistance of the electrolyte becomes increasingly important in determining the magnitude and distribution of current and potential in electrolysis as the size of the cell is increased; polarisation becomes increasingly important as the size is decreased. A more quantitative treatment, for a simple type of cell, is given in the following paper. It is there shown that a certain length, χ, may be defined in terms of the specific conductivity of the electrolyte and the slope of the polarisation curve, and the relative importance of polarisation and resistance of electrolyte in any cell depends on the ratio of χ to the linear dimensions of the cell.

Conditions for "True" Model Experiments.

We have so far postulated that the specific conductivity, κ, has the same value in the large cell A as in the small cell B; we now consider simultaneous variation in κ and in the size of cell.

It has already been mentioned that, if B is a true model of A, the current densities and potentials must be the same at corresponding points in the cells A and B. It follows that V_a, and E_1 and E_2 (at corresponding points P and Q) must also be the same in the two cells. Under these conditions, (4) is satisfied for both cells provided the ratio l/κ remains constant, i.e. provided the specific conductivity of the electrolyte is proportional to the linear dimensions of the cell and electrodes. This is the essential condition for geometrically similar cells of different sizes to be true models of one another. In practice, the required change in κ can readily be brought about by changing the concentration of the solution.

It is, however, important that the available voltage and the polarisation curves should not be changed thereby, since it has been implicitly assumed above that V_a, E_1 and E_2 have the same values in both cells if the current densities remain the same. It seems likely that changes in concentration of the electrolyte will not have much effect on diffusion phenomena involving uncharged solutes such as oxygen, which are an important factor in the cathodic polarisation in most corrosion systems. Polarisation of the anodes in corrosion sometimes arises from the resistance of pores in an oxide-film. If these pores are filled with the main electrolyte, the polarisation curve will change considerably with the concentration and true model experiments will be impossible; if, on the other hand, they are filled with a solution of a salt of the underlying metal, the change will probably be slight.

The dependence of E_1, E_2 and V_a on concentration can be determined experimentally, and the possibility of adjusting the conditions in the two cells so as to allow for any observed change must be considered. It is doubtful whether any such adjustment will generally be possible as far as changes in the polarisation are concerned, owing to the complicated nature of such changes. But in some cases it would be possible to allow for changes in V_a by introducing an additional E.M.F. at some point in the metallic part of the circuit.

This analysis was prompted by researches carried out in the Corrosion Res. Section, Cambridge, and we are much indebted to Dr. U. R. Evans for his constant interest and support.

Summary.

Consideration of two cells having the same electrolyte and electrodes, but differing in size, shows that they are not, in general, true models of

one another, as regards the magnitude and distribution of current and potential. In very large cells, the resistance of the electrolyte becomes the most important factor, while in very small cells electrode polarisation is predominant. Two cells of different sizes may be true models of one another provided the specific conductivity of the electrolyte is made proportional to the linear dimensions.

Résumé.

Considérant deux cellules avec le même électrolyte et les mêmes électrodes, mais de tailles différentes, on montre qu'elles ne se comportent pas, en général, de façon absolument identique en ce qui concerne la grandeur et la répartition de l'intensité et du potentiel. Dans de très grandes cellules, la résistance de l'électrolyte devient le facteur essentiel, tandis que dans des cellules très petites, la polarisation à l'électrode prédomine. Deux cellules de tailles différentes peuvent se comporter de façon tout à fait identique, si l'on choisit deux électrolytes tels que les conductivités spécifiques sont proportionnelles aux dimensions respectives.

Zusammenfassung.

Ein Elektrolysierbad, das dieselbe Elektrolytlösung und gleichartige Elektroden wie ein zweites enthält, aber verschieden gross ist, ist im allgemeinen nicht ein getreues proportionelles Abbild dieses zweiten Gefässes, was die Grösse und Verteilung von Strom und Ladung anbelangt. In sehr grossen Gefässen ist der Widerstand der Elektrolytlosung der bedeutendste Faktor, während in kleinen Gefässen die Elektrodenpolarisation am wichtigsten ist. Das oberwähnte Abbild ist nur dann getreu, wenn die spezifischen Leitfähigkeiten der Elektrolyte in den zwei Bädern den linearen Dimensionen der Gefässe proportional gemacht werden.

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FACTORS IN THROWING POWER ILLUSTRATED BY POTENTIAL-CURRENT DIAGRAMS.

BY T. P. HOAR AND J. N. AGAR.

Received 13th March, 1947.

The "throwing power" of an electroplating bath is qualitatively well understood; a bath has good throwing power if it is possible to deposit a reasonably even coating on a cathode of irregular shape, without recourse to shaped anodes or other geometrical devices. It is also well known that good throwing power is favoured by low electrolytic resistance and by high cathodic polarisation—though as will appear, the latter term requires more exact definition than it is usually given. Throwing power has been estimated quantitatively by a number of experimental methods, all of which are necessarily simplifications of the complex conditions occurring in practice; that due to Haring and Blum [1] is the best known, and is the one we shall discuss.

Potential-current diagrams have been used to illustrate and clarify *inter alia* cathodic efficiency and resistance losses in electroplating,[2] the

[1] Haring and Blum, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 313.
[2] Field, *The Principles of Electrodeposition* (Pitman, 1944).

mechanism of film breakdown and repair on corroding metals,[3] the velocity of metallic corrosion,[4, 5, 6] the mechanism of corrosion inhibitors and accelerators,[7] cathodic protection,[8] and the electrochemistry of bi- and tri-metallic corroding systems such as arise in cases of metallic coatings on metals[9, 10] and of zinc protectors as applied to ships' hulls.[11] They do not, however, appear to have been hitherto applied to throwing power.

Gardam[12] has discussed throwing power, as estimated by the Haring Cell technique,[1] analytically without reference to potential-current diagrams. The following analysis is partly similar to Gardam's, but taken in conjunction with the diagrams gives perhaps a more vivid picture of the factors that influence throwing power.

The Haring Cell arrangement is shown in Fig. 1. Two electrically connected cathodes are disposed at the square ends of a rectangular box. The gauze anode is arranged further from one cathode than the other, so that when electrolysis occurs, the further cathode at distance l_1 cm. carries less current and receives a lighter deposit, m_1 g., than that, m_2 g., received by the nearer cathode at distance l_2 cm. If the "length ratio" in the cell is $l_1/l_2 = L$ and the "metal ratio" is $m_2/m_1 = M$, throwing power T may be expressed[2] numerically by

$$T = \frac{L - M}{L + M - 2} \times 100. \quad \quad (1)$$

Thus when the far cathode receives a metal deposit equal to that received by the near, $M = 1$ and the throwing power is 100; when $M = L$, the throwing power is 0; and when there is *no* deposit on the far cathode, $M = \infty$ and the throwing power is -100.

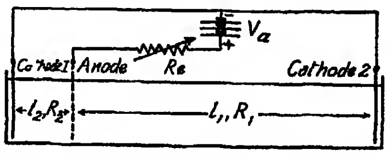

FIG. 1.—Haring cell for estimation of throwing power.

We shall first assume that the metal ratio m_2/m_1 is equal to the cathodic current ratio, i.e. that the cathodic current efficiency is the same at the two different cathodic current densities. We shall also assume that the electrolytic resistances of the alternative current paths are proportional to the distances l_1 and l_2.

Let

I_1 be the current in amp. flowing to the far cathode,

I_2 the current in amp. flowing to the near cathode,

E_{c_1} the "single potential" in volts of the far cathode on the hydrogen scale (i.e. the potential difference between points on either side of and close to the metal-solution interface, the single potential of the normal hydrogen electrode being taken as 0 and the single potentials of noble metals being reckoned positive),

E_{c_2} the single potential in volts of the near cathode,

E_A the single potential in volts of the anode,

V_a the E.M.F. in volts of the d.c. source,

R_1 the electrolytic resistance in ohms between the far cathode and the anode,

[3] Bannister and Evans, *J. Chem. Soc.*, 1930, 1361.
[4] Evans, *J. Franklin Inst.*, 1929, **208**, 45.
[5] Evans and Hoar, *Proc. Roy. Soc. A*, 1932, **137**, 343.
[6] Brown and Mears, *Trans. Electrochem. Soc.*, 1938, **74**, 495.
[7] Hoar, *Chim. Ind.*, 1939, **41**, 118.
[8] Mears and Brown, *Trans. Electrochem. Soc.*, 1938, **74**, 519.
[9] Hoar, *J. Electrodepositors' Tech. Soc.*, 1938, **14**, 33; *Met. Ind.* (*Lond.*), 1937, **51**, 649; 1938, **52**, 87.
[10] Hoar, *Nature*, 1946, **157**, 408.
[11] Hoar (unpublished work), 1943.
[12] Gardam, *Trans. Faraday Soc.*, 1938, **34**, 698.

R_2 the electrolytic resistance in ohms between the near cathode and the anode, and

R_e the external resistance in ohms in series with the d.c. source and the electrodes.

The relationships between these magnitudes are illustrated in Fig. 2. AG is the E_c/I curve for either cathode; if we select the metal of the two cathodes as a point of zero potential, E_{c_1} and E_{c_2} are the potentials of points in the electrolyte adjacent to the far and near cathodes respectively. AH is the curve for the anode; in order to bring it into the correct relationship with the E_c curve for the cathodes, each point on it must be shifted downwards through a distance $V_a - IR_e$ to allow for the applied E.M.F., V_a, and for the fall of potential across the external resistance R_e due to the current I. This gives the line BJ, and we are interested in the point on it representing a total current $(I_1 + I_2)$ and the potential of the electrolyte adjacent to the anode, $E_A - \{V_a - (I_1 + I_2)R_e\}$. The fall of the potential across the electrolyte between the far cathode and the anode is thus $E_{c_1} - E_A - \{V_a - (I_1 + I_2)R_e\}]$, and the fall between the near cathode and the anode is $E_{c_2} - [E_A - \{V_a - (I_1 + I_2)R_e\}]$. The resistances R_1, R_2, in Fig. 2 and the following diagrams, are equal to the slopes of the lines OP, OQ, etc.; they are throughout drawn with a ratio of slope of 5 : 1, since this is the usual length ratio in the Haring cell.

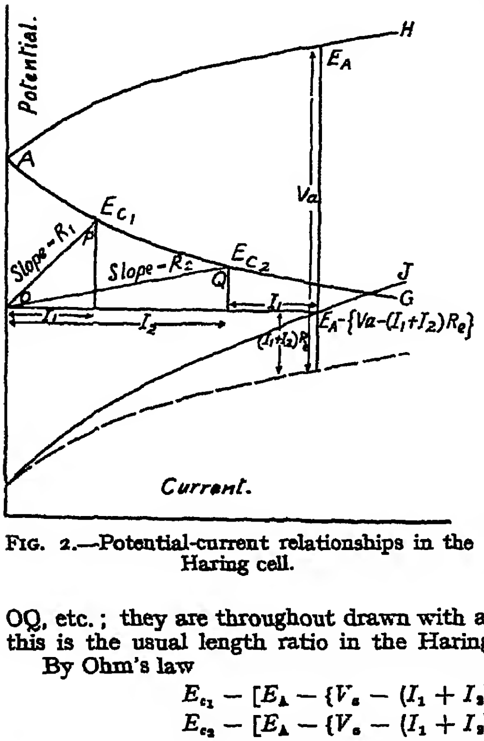

FIG. 2.—Potential-current relationships in the Haring cell.

By Ohm's law

$$E_{c_1} - [E_A - \{V_a - (I_1 + I_2)R_e\}] = I_1R_1,$$
$$E_{c_2} - [E_A - \{V_a - (I_1 + I_2)R_e\}] = I_2R_2.$$

Thus

$$E_{c_1} - E_{c_2} = I_1R_1 - I_2R_2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$\frac{(E_{c_1} - E_{c_2})}{(I_2 - I_1)} = \frac{I_1R_1 - I_2R_2}{(I_2 - I_1)} = \frac{R_1 - \left(\frac{I_2}{I_1}\right)R_2}{\left(\frac{I_2}{I_1}\right) - 1},$$

whence

$$\frac{I_2}{I_1} = \frac{R_1 + (E_{c_1} - E_{c_2})/(I_2 - I_1)}{R_2 + (E_{c_1} - E_{c_2})/(I_2 - I_1)} \quad . \quad . \quad . \quad . \quad (3)$$

By dividing both sides of (2) by $(I_1 + I_2)$ instead of by $(I_2 - I_1)$ we obtain

$$\frac{I_2}{I_1} = \frac{R_1 - (E_{c_1} - E_{c_2})/(I_1 + I_2)}{R_2 + (E_{c_1} - E_{c_2})/(I_1 + I_2)} \quad . \quad . \quad . \quad (4)$$

an equation equivalent to that obtained by Gardam.[12]

We thus obtain the cathodic current ratio I_2/I_1 in terms of the electrolytic resistances, R_1, R_2, the difference of the single potentials of the

cathodes, $E_{c_1} - E_{c_2}$, and either the difference between or the sum of the cathodic currents I_1 and I_2. Gardam, using his equation equivalent to (4), points out that the current ratio depends on the total current, which is equal to twice the mean cathodic current. Equation (3), however, bringing in the *difference* between the two cathodic currents, is yet more revealing; it may be written

$$\frac{I_2}{I_1} = \frac{R_1 - \Delta E_c/\Delta I}{R_2 - \Delta E_c/\Delta I} \quad . \quad . \quad . \quad . \quad (3a)$$

where ΔE_c is the increase in E_c (actually always negative), and ΔI the increase in I, as we pass from cathode 1 to cathode 2. Now $\Delta E_c/\Delta I$ is a magnitude of fundamental importance: it is approximately equal to dE_c/dI for the E_c/I curve over the range E_{c_1} to E_{c_2}, being of course exactly equal to dE_c/dI if the curve is rectilinear.

The current ratio I_2/I_1, which (if we assume constant cathodic current efficiency) decides the throwing power, therefore depends upon the resistances R_1 and R_2 and upon the slope of the E_c/I curve. Evidently, increase of $-\Delta E_c/\Delta I$ relative to R_1 and R_2 decreases I_2/I_1 down to a limit of 1 (perfect throwing power), while decrease of $-\Delta E_c/\Delta I$ increases I_2/I_1 up to a limit of R_1/R_2 (no throwing power). In general, if we define throwing power T by (1) and take $M = m_2/m_1 = I_2/I_1$, we readily obtain

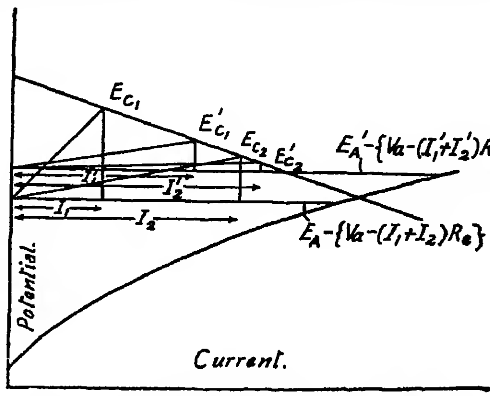

FIG. 3.—Influence of electrolytic resistance.

$$T = \frac{1}{1 - 2R_2\bigg/\dfrac{\Delta E_c}{\Delta I}} \times 100 \quad . \quad . \quad . \quad . \quad (5)$$

giving a variation of T from 0 to 100 as $\Delta E_c/\Delta I$ varies from 0 to $-\infty$. This equation is general whatever the form of the E_c/I relationship; the equivalent equation obtained by Gardam [18] contains dE_c/dI instead of $\Delta E_c/\Delta I$, and is thus valid only for a rectilinear E_c/I curve.

Several particular cases may be illustrated graphically.

(i) Influence of Electrolytic Resistance.—Fig. 3 shows the effect of diminishing R_1 and R_2 sixfold to R_1' and R_2', when $\Delta E_c/\Delta I$ remains constant; the current ratio is decreased from I_2/I_1 to I_2'/I_1'. This effect is obtained in practice by adding a non-depositing salt such as sodium chloride to a plating bath to increase conductivity.

(ii) Influence of Cathodic Polarisation.—It is commonly stated that good throwing power, i.e. $I_2/I_1 \rightarrow 1$, is favoured by "large cathodic polarisation". This is inexact. Cathodic polarisation is, properly, the change in single potential of an electrode when it is polarised cathodically. We have shown, however, that the interesting function is the ***increment*** of cathodic polarisation relative to the increment of cathodic current as we pass from the far to the near cathode—that is, the mean gradient of the cathodic polarisation curve between the current values I_1 and I_2. When this gradient is small, I_2/I_1 approaches R_1/R_2 (Fig. 4*a*); when it is large, I_2/I_1 approaches 1 (Fig. 4*b*). General increase of gradient of cathodic polarisation curves, and consequent better throwing power, is

obtained in practice by the use of addition agents, and/or by depositing from a complex-ion electrolyte; it is also favoured by low temperature.

(iii) Influence of Total Current.—The total current $(I_1 + I_2)$ for a given electrolyte in a Haring Cell may be increased either by increasing

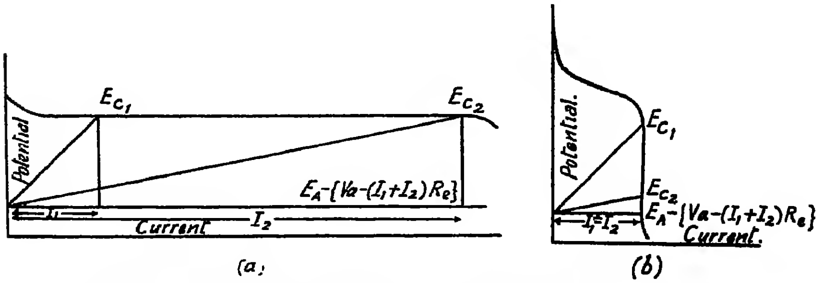

FIG. 4(*a*) and (*b*).—Influence of slope of cathodic polarisation curve.

the E.M.F., V_a, of the d.c. source (as with a variable transformer-rectifier source) or by decreasing the external resistance R_e. Fig. 5 shows the effect of increasing $(I_1 + I_2)$ by increasing V_a/R_1, R_2 and R_e remaining constant; a general form of cathodic E_c/I curve is illustrated. It is evident that increase of $(I_1 + I_2)$ influences I_2/I_1 only in so far as it leads to different values of $\Delta E_c/\Delta I$. In the case illustrated, the first increase of I_1 and I_2 to I_1' and I_2' (to the region where $\Delta E_c/\Delta I$ is small) leads to an increase of current ratio, while the further increase to I_1'' and I_2'' (to the region where $\Delta E_c/\Delta I$ is again large, due, for example, to concentration polarisation at high currents) leads to a decrease of current ratio.

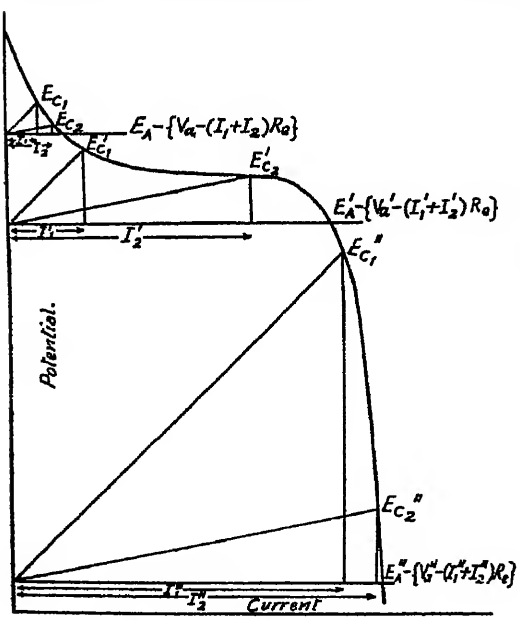

FIG. 5.—Influence of total current.

(iv) Influence of Cathodic Current Efficiency.—The assumption we have so far made, that the current ratio I_2/I_1 in the Haring Cell is equal to the metal-deposition ratio m_2/m_1, is not generally exact, since the efficiency of the metal deposition generally varies with current density. If C_1 and C_2 are the cathodic current efficiencies at the far and near cathodes respectively (i.e., the fractions of the cathodic currents that are accounted for by metal deposited), then

$$C_1 I_1 = \frac{m_1 F}{tJ} = I_{m_1}, \text{ and } C_2 I_2 = \frac{m_2 F}{tJ} = I_{m_2},$$

where F is Faraday's number, t sec. the time of current flow, J the equivalent

weight of the metal and I_{m_1}, I_{m_2} amp. are the currents equivalent to the metal deposition. Thus, from (3) and (3*a*),

$$\frac{m_2}{m_1} = \frac{I_{m_2}}{I_{m_1}} = \frac{C_2 I_2}{C_1 I_1} = \frac{C_2}{C_1} \cdot \frac{R_1 - \Delta E_c/\Delta I}{R_2 - \Delta E_c/\Delta I} \quad . \quad . \quad . \quad (7)$$

Alternatively, from (2),

$$E_{c_1} - E_{c_2} = I_1 R_1 - I_2 R_2 = \frac{I_{m_1} R_1}{C_1} - \frac{I_{m_2} R_2}{C_2},$$

and by the method used for obtaining (3) and (3*a*) we thus have

$$\frac{m_2}{m_1} = \frac{I_{m_2}}{I_{m_1}} = \frac{R_1/C_1 - \Delta E_c/\Delta I_m}{R_2/C_2 - \Delta E_c/\Delta I_m} \quad . \quad . \quad . \quad (8)$$

This last expression gives the metal-deposition ratio in terms of the resistances, the current efficiencies and $\Delta E_c/\Delta I_m$, the last term being evidently related to the true metal-deposition polarisation curve in exactly the same way as $\Delta E_c/\Delta I$ is related to the *total* cathodic polarisation curve. This is illustrated in Fig. 6. If we are, from the practical point of view, more interested in m_2 m_1 than in I_2 I_1, we should focus attention on (7) or (8) rather than on (3), and on the geometry of the metal-deposition polarisation curve as well as that of the total cathodic polarisation curve. The influence of change of cathodic current efficiency on m_2/m_1 is clear; $C_1 > C_2$ is the favourable condition for the reduction of m_2/m_1 towards the ideal value of unity, a fact well appreciated in practice.

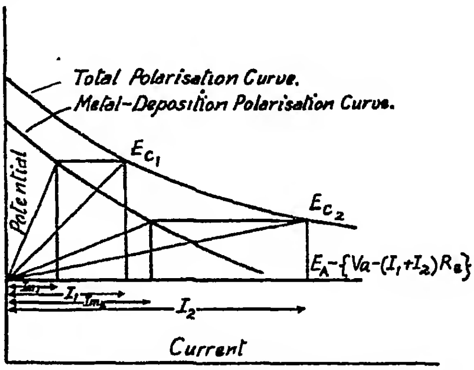

FIG. 6.—Influence of cathodic current efficiency.

It is not possible to obtain a simple expression for throwing power T, equivalent to (5), for this case where $m_2/m_1 \neq I_2/I_1$, and we must be content with the two alternative expressions for m_2/m_1 given in (7) and (8).

(v) Influence of Size.—The influence of the size of the Haring Cell may be obtained by transforming (3) into terms of current density i amp./cm.^{2}, and specific conductivity κ mhos/cm. If l_1, l_2 cm. are the lengths of the two electrolyte paths and A cm.^{2} is the area of each electrode,

$$R_1 = l_1/A\kappa, \qquad R_2 = l_2/A\kappa$$

and

$$I_1 = i_1 A, \qquad I_2 = i_2 A.$$

Thus

$$\frac{i_2}{i_1} = \frac{l_1 - \kappa\,\Delta E_c/\Delta i}{l_2 - \kappa\,\Delta E_c/\Delta i} = \frac{l_1 + \chi}{l_2 + \chi}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $\chi = -\kappa\,\Delta E_c/\Delta i$ and is dimensionally a *length*. This is the most fundamental form of the current-ratio equation, because $\Delta E_c/\Delta i$ does not depend on the area of the electrodes, whereas $\Delta E_c/\Delta I$, of course, does.

In a very large cell, where l_1 and l_2 are much greater than χ, $i_2/i_1 \sim l_1/l_2$ —in other words, the throwing power tends to zero; for an infinitely small cell, on the other hand, $i_2/i_1 = 1$ and the throwing power is 100. This point is of practical interest, since it clearly shows that a large-scale industrial plating bath will have poorer throwing power than a small experimental bath using the same electrolyte and the same current density. It is evident from (9) that the only way in which throwing power may be

maintained, as we pass from smaller to larger scale, is to make κ proportional to l_1 and l_2; that is, specific conductivity must be increased proportionately to size.

The present case is thus an example of the general argument concerning linear dimensions given in the preceding paper,[13] and, in a system of such simple geometry as the Haring Cell, that argument may be developed more quantitatively. It has already been mentioned that $\chi = - \kappa\, \Delta E_c/\Delta i$ is a length, and it is clear that χ represents the ratio of the mean slope of the polarisation curve to the specific resistance of the electrolyte, $1/\kappa$. Inspection of (9) shows that the current-ratio is mainly governed by the lengths of the current paths in the electrolyte, l_1 and l_2, (i.e., by the resistance of the electrolyte) when l_1 and l_2 are greater than χ. Conversely, the current-ratio is mainly determined by polarisation when l_1 and l_2 are less than χ. It is also clear from (9) that the actual current-ratio in the Haring Cell (with real, polarisable electrodes) is the same as that which would be observed in a cell fitted with ideal, non-polarisable electrodes at distances $l_1 + \chi$ and $l_2 + \chi$, instead of l_1 and l_2. In other words, the effect of polarisation on the distribution may be simulated by adding * a distance χ to the lengths of the actual current paths in the electrolyte and treating the electrodes as non-polarisable.

An exact discussion of cells and electrode systems more complicated than the Haring cell cannot be given in simple terms, but an *estimate* of the relative importance of polarisation and resistance of the electrolyte can be made in a similar manner, i.e., by considering the ratio of χ to the appropriate linear dimension.

Summary.

The relationships between current, potential and resistance for the Haring throwing-power cell are derived, and illustrated by means of potential/current diagrams. The influence of electrolytic resistance, cathodic polarisation, cathodic current density, cathodic current efficiency and size of the cell are evaluated and discussed.

Résumé.

On établit et illustre par des diagrammes potentiel-intensité, les relations entre intensité, potentiel et résistance dans la cellule de Haring pour l'étude du pouvoir couvrant. On évalue et discute l'influence de la résistance électrolytique, celle de la polarisation cathodique, de la densité de courant cathodique, de l'efficacité cathodique par rapport à l'intensité, enfin celle de la taille de la cellule.

Zusammenfassung.

Die Relationen zwischen Stromstärke, Spannung und Widerstand bei der Haring'schen Messmethode werden abgeleitet und mit Hilfe von Spannung-Stromstärkekurven dargestellt. Der Einfluss des elektrolytischen Widerstandes, der Polarisation, Stromdichte und Stromauswertung an der Kathode und der Grösse des Messgefässes werden berechnet und besprochen.

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[13] Agar and Hoar, *this vol.*, p. 158.
* χ is positive since $\Delta E_c/\Delta_i$ is negative.

OVERVOLTAGE IN METAL DEPOSITION AND DISSOLUTION.*

I.—NICKEL.

By F. W. Salt.

Received 18th March, 1947.

The electronic interrupter devised by Hickling [1] has been used to study the decay of the polarisation [2] which accompanies the electrolytic deposition and dissolution of nickel, and to determine the polarisation free from resistance error. The influence of current density, p_H, buffering agents, nickel-ion activity, and temperature on the polarisation and its decay has been investigated.

Experimental.

(a) Cathodic Polarisation.—Electrolyses were carried out in a 150 ml. tall Pyrex beaker fitted with a rubber bung carrying a thermometer, hydrogen delivery tube, Luggin capillary, anode compartment—a glass tube, 1 cm. diam., with the lower end closed by a filter-paper plug—and the cathode—a disc, 1·13 cm. diam., of pure nickel foil welded to a nickel wire which was fixed in a glass tube with sealing-wax. There was a length of about 2 cm. of wire between the foil and the tube ; the side of the foil to which the wire was attached and the exposed wire were insulated with Necol varnish, leaving a cathode area of 1 sq. cm. The same cathode was used repeatedly unless the deposit from a previous electrolyte was rough or exfoliated. A spiral of platinum wire, 1 sq. cm. in area, sealed into a glass tube, formed the anode ; the level of the anolyte was maintained below that of the catholyte. To keep the temperature of the electrolyte constant (within $\pm$ 0·5° c.), the cell was suspended within a 800 ml. beaker which contained water heated by a microburner. The solid constituents of the electrolyte were dissolved separately, and the solutions were filtered, boiled, cooled, and mixed. Ammonium hydroxide was added either as the concentrated solution (0·88 s.g.), or suitably diluted with air-free water. All reagents were of " Analar " grade, and were used without further purification ; the nickel content of the solutions was checked by analysis. The p_H of the solutions was measured with a Cambridge p_H meter ; the values are quoted to the nearest 0·1 unit only, because changes of that order occurred after electrolyses at high c.d. in some electrolytes.

Hydrogen from a cylinder was passed, for 2 hrs. before electrolyses commenced, first through a portion of the electrolyte in a Drechsel bubbler, and then through the main electrolyte ; it escaped through a small hole in the wide portion of the Luggin capillary in which rested one limb of an inverted *U*-tube filled with saturated potassium chloride solution and closed with filter-paper plugs. A loose rubber sleeve which fitted round

* Communication from the Armament Research Department, Ministry of Supply.

[1] *Trans. Faraday Soc.*, 1937, **33**, 1540.

[2] The literature of metal overvoltage in general has been reviewed recently by Ioffe (*Uspekhi Khim.*, 1943, **12**, 438) and Butler (*Electrocapillarity*, 1940, 166). Experimental investigations of nickel overvoltage during the past twenty years include those of Makar'eva (*Bull. Acad. Sci. U.R.S.S.*, 1941, 573), Verdieck, Ksycki and Yntema (*Trans. Amer. Electrochem. Soc.*, 1941, **80**, 41) ; Yuza and Kopyl (*J. Physic. Chem.* (*Russ.*), 1940, **14**, 1074) ; Essin and Loschkarev (*ibid.*, 1939, **13**, 186) ; Foerster and Georgi (*Z. physik. Chem.* (Bodenst. Fest.), 1931, 453) ; Erdey-Grúz and Volmer (*ibid.*, 1931, **157**, 165) ; Isgarischev and Ravikovitsch (*ibid.*, 1929, **140**, 235) ; O'Sullivan (*Trans. Faraday Soc.*, 1930, **26**, 533) ; and Glasstone (*J. Chem. Soc.*, 1926, 2887).

the limb, and over the open end of the Luggin capillary, retarded the ingress of air while permitting the escape of hydrogen. The *U*-tube made contact with a saturated calomel reference electrode via a beaker containing a saturated solution of potassium chloride ; and to minimise contamination of the electrolyte with chloride ions, the tube was inserted in the Luggin capillary only just before measurements were made. The capillary tip, which was ground to an angle of 45° with the slope uppermost so that hydrogen bubbles could not enter the capillary and break the cathode/reference-electrode circuit, pressed lightly against the centre of the cathode. Throughout the passage of hydrogen, the cathode was immersed in the electrolyte ; it had previously been degreased by cathodic polarisation at 0·05 amp./sq. cm. in a solution containing 50 g. each per litre of NaOH and $Na_2CO_3 . 10H_2O$, and then lightly etched by anodic polarisation at 0·2 amp./sq. cm. in a solution containing 200 ml. of H_2SO_4 (S.G. 1·84) per litre. This was followed by a few sec. of cathodic polarisation at the same c.d. in another portion of the acid.

Before the main set of measurements was made, trial polarisations were carried out in succession at 10^{-4}, 10^{-3}, and 10^{-2} amp./sq. cm. in each electrolyte ; the polarising currents were checked by measuring the p.d. across a standard resistor with a Cambridge valve potentiometer. Measurements were not recorded until the cathode/reference-electrode e.m.f. became constant ; this condition was usually attained after polarisation for 5-10 min. The e.m.f. was read, to the nearest 0·002 v., on a Cambridge Unipivot meter arranged as a potentiometer-voltmeter to supply an equal opposing e.m.f. in the grid circuit of a thyratron which had a loudspeaker in its anode circuit as a null-point indicator. Particularly at 10^{-1} amp./sq. cm., and at lower c.d. with M./20 nickel sulphate solutions, readings of the e.m.f. at the various periods of interruption were taken as rapidly as possible to minimise changes in the cathode surface and in the composition of the electrolyte. It was noted that, even at the longest period of interruption (*ca.* 10^{-1} sec.) of the polarising current, the e.m.f. was unaffected by the bubbling of hydrogen through the electrolyte. When a set of readings for the decay of the e.m.f. had been obtained, the current was switched off ; and after waiting for a period (usually about 100 sec.) which depended upon the polarising c.d. and the duration of the electrolysis, the constant, static e.m.f. was observed. The current was then switched on again, adjusted to the next higher value, and a further series of measurements was made. To determine the overvoltage of nickel deposition at a given instant during its decay, the static cathode/reference-electrode e.m.f. was subtracted from the e.m.f. measured at the end of this period of interruption of the electrolysis. As a check on the interrupter method, measurements by the " direct method " were obtained by switching-off the interrupter and using the thyratron potentiometer alone.

The interrupter was fundamentally the same as the one previously used for studying the decay of hydrogen overvoltage,[3] except that a smaller thyratron (GT1C, instead of GT5E) was used and very short periods of interruption could be obtained by allowing a 0·01, instead of 0·5, μF capacitor * to discharge through the thyratron and the series of resistors. It was desired to measure the cathode/reference-electrode e.m.f. 5×10^{-6} sec., at the latest, after the polarising current had been interrupted ; because Frumkin[4] has criticised the extrapolation method used by Hickling and Salt[5] to obtain the value at the instant of current interruption on the ground that the polarisation may decay by 0·1-0·2 v. during the first 5×10^{-6} sec. In the study of hydrogen overvoltage, measurements at periods shorter than that were not made ; for when the interrupter was tested by means of the circuit shown in Fig. 1, the minimum

* The 0·5 μF. capacitor was used for periods greater than 3×10^{-5} sec.

[3] Hickling and Salt, *Trans. Faraday Soc.*, 1941, **37**, 450.

[4] *Acta Physicochim.*, 1943, **18**, 23.

[5] *loc. cit.*

e.m.f. of the standard cell and the potential drop across R combined exceeded that of the cell when the current was interrupted for less than 5×10^{-5} sec. At the shorter periods available with the present interrupter, very high residual voltages * were observed; e.g. when R (Fig. 1) was a 10 ohm resistor consisting of approximately 18 cm. of 34 S.W.G. nichrome wire, insulated, and doubled along most of its length, the minimum p.d. given in Table I were observed when a current of 0·1 amp.† was passed through it; the standard cell was omitted. It is unlikely that the residual voltage is due to the inductance of the 10 ohm resistor; for this is of the order of 10^{-7} henry only, whereas it would need to be about 10^{-3} henry to account for the p.d. observed. When a capacitor is connected across the resistor, however, the residual voltage is apparently considerably lowered; because in calibrating [6] the interrupter, the points for the shortest periods of interruption lie fairly close to a straight-line graph of resistance in the interrupter thyratron circuit against period of interruption. If the observed periods are corrected on the basis of

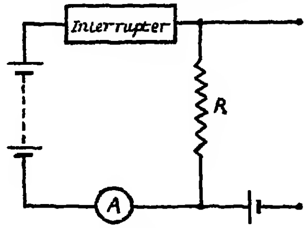

FIG. 1.

TABLE I.

Period of interruption (sec. $\times 10^{-6}$)	1·3	3·2	6·7	15	27	66	140
P.D. across R (volt)	0·75	0·435	0·25	0·105	0·055	0·01	0·00

Table I, their plot becomes a curve (Fig. 2). This effect of capacitance probably accounts for the fact that extrapolations of η-i graphs for a nickel electrode at 10^{-1} amp./sq. cm. are within 1-2 centivolts of the direct values.

(b) Anodic Polarisation.—The experimental technique differed from that described in (*a*) in two respects: the chloride electrolyte was not saturated with hydrogen, and the nickel electrode was built-up prior to use as an anode by deposition of nickel at a c.d. of 0·01 amp./sq. cm. for 24 hr. from a solution containing $NiSO_4 . 7H_2O$, 140; $(NH_4)_2SO_4$, 22; KCl, 8; and NH_4OH 0·59 g./l.; p_H 5·6, $T = 35°$. The connections to the cell were, of course, reversed so that the Pt spiral in the 1 cm. tube plugged with filter paper became the cathode. It was found that the residual polarisation at the anode after the longest period of interruption was

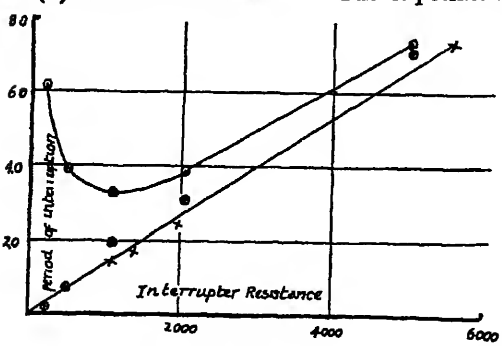

FIG. 2.
(⊙ = ohms, × = ohms × 10).

* They were not, apparently, due to delayed response of the indicator thyratron owing to its 10^{-6} sec. breakdown-time (Snoddy, *Physics*, 1933, 4, 366); for residual voltages of the same order were recorded with a double triode trigger-circuit (Starr, *Wireless Eng.*, 1935, 12, 601).

† Almost identical p.d. were observed with a current of 0·01 amp. and R = 100 ohm.

[6] See ref.[5], p. 453.

TABLE II.

pH.	Buffering Agents.*	M./2 $NiSO_4$—Cathodic overvoltage (volt) at 0·1 amp./sq. cm.														
		Direct Value.	Period of Decay (sec. × 10^{-3}).													
			0·318	0·665	1·45	2·71	6·98	14·0	34·9	69·8	146	377	779	1390	3160	3540
	$T = 35°$.															
2·1	M./25 H_2SO_4 + M./6 $(NH_4)_2SO_4$	0·74	0·515	0·44	0·40	0·385	0·38	0·375	0·365	0·36	0·35	0·345	—	0·34	0·31	0·29
2·3	M./6 NaH_2 citrate	0·56	0·50	0·45	0·41	0·39	0·385	0·38	—	0·38	0·38	—	—	0·38	0·36	0·355
3·1	M./6 $NaCO_2H$ + M./6 H . CO_2H	0·41	0·37	0·33	0·31	0·30	0·295	—	—	0·295	—	—	0·29	0·28	0·255	0·24
4·4	M./3 NaOAc + M./6 H . OAc	0·50	0·445	0·395	0·365	0·355	0·355	0·345	0·34	0·32	0·295	0·255	0·23	0·215	0·195	0·19
5·5	M./5 NH_4OAc	0·475	0·465	0·44	0·415	0·405	0·40	—	—	0·39	0·375	0·35	0·335	0·32	0·28	0·26
6·2	M./5 NH_4OAc + M./25 NH_4OH	0·455	0·435	0·41	0·385	0·375	0·375	—	—	0·37	—	0·365	0·325	0·305	0·27	0·26
6·7	M./5 NH_4OAc + M./5 NH_4OH	0·38	0·37	0·34	0·315	0·30	0·30	—	—	0·30	—	—	—	—	0·295	0·235
7·2	M./5 NH_4OAc + M./2 NH_4OH	0·42	0·405	0·38	0·355	0·34	0·34	—	—	0·34	0·34	0·335	0·325	0·315	0·30	0·29
7·9	M./5 NH_4OAc + M. — NH_4OH	0·41	0·395	0·38	0·36	0·345	0·345	—	—	0·345	0·34	0·335	0·32	0·31	0·30	0·285
8·9	M./5 NH_4OAc + 2M. — NH_4OH	0·46	0·455	0·445	0·43	0·42	0·42	—	—	0·415	0·405	0·395	0·385	0·375	0·34	0·33
5·6	M./6 $(NH_4)_2SO_4$ + M./60 NH_4OH	0·49	0·485	0·47	0·45	0·44	0·44	—	0·44	0·41	0·375	0·36	0·325	0·285	0·24	0·22
5·9	M./6 $(NH_4)_2SO_4$ + M./30 NH_4OH	0·495	0·485	0·47	0·45	0·44	0·44	—	0·425	0·395	0·37	0·36	0·335	0·295	0·26	0·245
6·5	M./6 $(NH_4)_2SO_4$ + M./6 NH_4OH	0·485	0·48	0·46	0·44	0·425	0·425	0·425	—	0·42	0·41	0·38	0·35	0·34	0·29	0·275
7·0	M./6 $(NH_4)_2SO_4$ + M./3 NH_4OH	0·46	0·45	0·435	0·42	0·41	0·41	—	0·40	0·39	0·36	0·335	0·31	0·275	0·23	0·21
7·6	M./6 $(NH_4)_2SO_4$ + M. — NH_4OH	0·42	0·415	0·41	0·40	0·39	0·39	0·385	0·38	0·375	0·36	0·345	0·33	0·305	0·29	0·28
	$T = 25°$.															
5·6	M./5 NH_4OAc	0·65	0·57	0·525	0·495	0·48	0·48	—	—	0·47	0·445	0·41	0·39	0·37	0·34	0·33
6·8	M./6 $(NH_4)_2SO_4$ + M./6 NH_4OH	0·605	0·55	0·52	0·49	0·475	0·475	0·465	0·46	0·445	0·42	0·39	0·335	0·32	0·28	0·265
	$T = 45°$.															
5·4	M./5 NH_4OAc	0·535	0·50	0·47	0·44	0·42	0·42	0·42	—	0·39	0·37	0·325	0·29	0·28	0·25	0·23
		M./20 $NiSO_4$.														
	$T = 35°$.															
2·5	M./100 H_2SO_4 + M./6 $(NH_4)_2SO_4$	0·77	0·745	—	0·73	—	0·73	—	—	0·72	—	—	0·70	0·68	0·61	0·59
5·7	M./6 $(NH_4)_2SO_4$ + M./300 NH_4OH	0·76	0·66	0·61	—	0·56	—	—	—	—	0·56	—	—	0·56	0·46	0·46
6·5	M./6 $(NH_4)_2SO_4$ + M./60 NH_4OH	0·84	0·74	0·69	0·66	0·62	0·62	—	—	0·615	—	—	0·60	0·56	0·46	0·43
8·8	M./6 $(NH_4)_2SO_4$ + M./2 NH_4OH	0·715	0·60	0·565	0·54	—	0·54	—	—	0·54	—	—	0·525	0·49	0·385	0·37

* These are the same in Tables III and IV.

unaffected when the electrolyte was agitated by a vigorous stream of air. Even at the highest c.d. used (0·1 amp./sq. cm.), no evolution of gas from the anode was noticed.

Results and Discussion.

(a) Cathodic Polarisation.—Values of η at a series of intervals throughout its decay at c.d. of 0·1, 0·01, and 0·001 amp./sq. cm. are presented in Tables II and III which contain results for the effect of pH, buffering agents, temperature, and nickel-ion activity on the rate of decay. A table for 0·0001 amp./sq. cm. is not given, because in the range studied (0-0·1 sec), the overvoltage decayed (logarithmically) usually by only 0·01-0·05 v.; direct values of η_0 for this c.d. are included in Table IV. In Table II the decay series for pH 5·8 (35°) and pH 4·4 (25°) were omitted because the c.d. was uncertain owing to deposition of $Ni(OH)_2$ and basic Ni salts on the cathode. For most of the results at 0·001 and 0·01 amp./sq. cm., the course of the decay can be expressed precisely by the relation

$$\eta_t = \eta_0 - B \log (1 + Kt),$$

where the most frequently occurring values of K for 0·001 and 0·01 amp./sq. cm. are, respectively, 0·01 and 0·1 when t is expressed in units of 10^{-4} sec. The constants η_0 and B were evaluated by determining the regression line for each set of results. If the equation for the line is written $y = c + mx$, then

$$x = \log (1 + Kt),\ m = -B = \{\Sigma(\eta_t . x) - \Sigma\eta_t . \Sigma x/N\} \div \{\Sigma x^2 - (\Sigma x)^2/N\},$$

and $c = \eta_0 = (\Sigma\eta_t - m\Sigma x)/N$; N is the number (e.g. 10) of η_t/x pairs used in the calculation. Analysis of variance showed that the regression function was highly significant; e.g. with the pH 5·5 solution at 0·01 amp./sq. cm. to which the function $\eta_t = 0{\cdot}327 - 0{\cdot}104 \log (1 + 0{\cdot}1t)$ applies, F * is 144, whereas the 1 % point of F is 10 (for $N = 12$). The difference between calculated and observed values of η_t was seldom 0·01 v., and was usually only 0·001 – 0·003 v. The calculated values of η_0 and B for 0·001 and 0·01 amp./sq. cm. are listed in Table IV. (Where no indication is given K is 0·01 for 0·001 amp./sq. cm. and 0·1 for 0·01 amp./sq. cm.). Owing to the variation in K, the values for B cannot be used directly to compare the rates of decay in the different electrolytes; therefore the differential coefficients of the various functions have been obtained, and the values (in v./sec.) of $- d\eta/dt$ after the overvoltage has decayed for 10^{-4} sec. are given. For the electrolytes of pH 2·1, 2·3, and 3·1 at 0·001 amp./sq. cm. values of η_0 only are given; because the $\eta_t/\log (1 + 0{\cdot}01t)$ graphs consisted of two approximately parallel portions connected by a short line of steeper slope. A similar, though less marked, tendency was apparent with these electrolytes at 0·01 amp./sq. cm. With the electrolytes of pH 4·4 and 6·8 (25°), and 6·5 (M./20) at 0·01 amp./sq. cm., and pH 5·6, 7·0 and 7·6 at 0·001 amp./sq·cm., the decay graphs tended to become horizontal after $1 - 2 \times 10^{-3}$ sec. The graph for the pH 5·7 (M./20 $NiSO_4$) solution at 0·01 amp./sq. cm. (Fig. 3) was unique in resembling a typical graph for 0·1 amp./sq. cm. by having a well-defined constant voltage portion preceding the logarithmic decay.

At 0·1 amp./sq. cm. the decay in all electrolytes was characterised by an extremely rapid fall during the first 2×10^{-4} sec., followed by a halt in which the overvoltage remained practically constant for periods, depending on the electrolyte, of $3 - 300 \times 10^{-4}$ sec. The approximate periods, in units of 10^{-4} sec., at which the halts cease are given under t_L in Table IV, and the values of η during the halt are headed η_K. The subsequent decay, when the halt was sufficiently short to enable η_t to be measured at six or seven points on it, was found to give an accurate linear plot of η_t against log

* Goulden, *Methods of Statistical Analysis*, p. 269.

$(1 + t)$; the slopes of these lines are given under B (0·1 amp./sq. cm.) in Table IV. With the *p*H 2·5 (M./20) and 2·1 electrolytes the 'halt' was a slow (logarithmic) decay. It will be seen from Fig. 3 that, over part of the decay, the overvoltage at 0·1 amp./sq. cm. for the *p*H 5·7 (M./20) electrolyte

TABLE

*p*H.		M./2NiSO$_4$								
		Period of Decay (sec. × 10^{-4}). 0·001 amp./sq. cm.								
	Direct Value.	0·605	6·05	12·6	32·6	67·4	83·6	121	294	366
2·1	0·27	0·27	—	0·265	0·255	0·245	0·235	0·20	0·17	0·16
2·3	0·265	0·265	0·265	0·26	0·255	0·235	0·225	0·21	0·195	0·185
3·1	0·26	0·26	0·26	—	0·255	0·245	0·225	0·205	0·175	0·16
4·4	0·22	0·22	0·22	0·215	0·205	0·195	0·185	0·18	0·15	0·145
5·5	0·25	0·25	—	0·245	0·235	0·225	0·21	0·20	0·17	0·16
6·2	0·19	0·19	—	—	0·185	0·175	—	0·165	0·145	0·14
6·7	0·16	0·16	—	0·155	0·15	0·14	—	0·135	0·12	0·11
7·2	0·15	0·15	0·15	0·145	0·14	—	0·135	0·125	0·12	0·115
7·9	0·14	0·14	0·14	—	0·135	—	0·13	0·125	0·115	0·11
8·9	0·155	0·155	0·155	—	0·15	0·145	—	0·14	0·13	0·125
5·6	0·25	0·25	0·245	0·235	0·21	0·19	0·175	0·165	0·135	0·12
5·9	0·205	0·205	0·20	—	0·195	0·185	—	0·175	0·155	0·15
6·5	0·18	0·18	0·18	0·18	0·17	0·16	—	0·155	0·145	0·135
7·0	0·20	0·20	0·195	0·185	0·17	0·14	0·135	0·125	0·10	0·085
7·6	0·19	0·19	0·185	0·18	0·17	0·155	0·14	0·13	0·11	0·10
5·8*	0·185	0·185	0·185	0·18	0·17	0·155	—	0·14	0·12	0·11
4·4†	0·24	0·24	0·237	0·235	0·22	0·21	—	0·205	0·175	0·175
5·6	0·265	0·26	0·26	—	0·255	0·24	0·235	0·23	0·215	0·205
6·8	0·205	0·205	0·205	—	0·20	0·19	0·185	0·175	0·165	0·16
5·4	0·22	0·217	0·212	0·21	—	0·20	0·195	0·19	0·175	0·17
2·5	0·305	0·305	0·30	0·295	0·265	0·245	0·24	0·23	0·19	0·175
5·7	0·295	0·285	0·28	—	0·275	0·25	—	0·235	0·22	0·19
6·5	0·28	0·275	0·27	0·265	0·26	0·255	0·25	0·245	0·225	0·22
8·8	0·225	0·225	—	—	0·22	0·215	0·21	0·205	0·19	0·175

* Buffering agents: M./500 $Na_2B_4O_7$ + M./5 H_3BO_3.
† Buffering agents: M./3 NaOAc + M./6 HOAc.

falls below that for 0·01 amp./sq. cm.; this was unique in the cathodic polarisation.

Effect of Current Density.—In the electrolytes for which values of b are given in Table IV, the overvoltage varied with c.d. between 10^{-4} and 10^{-2} amp./sq. cm. according to the equation $\eta = a + b \log I$. With the others, upward curvature of the $\eta - \log I$ graph set in between 10^{-3} and 10^{-2} amp./sq. cm. All the graphs curved upwards between 10^{-2} and

10^{-1} amp./sq. cm. when the η_0 values at 10^{-1} amp./sq. cm. were those obtained by the direct method or by extrapolation of the $\eta - t$ graphs. This might be expected owing to concentration polarisation, since the limiting c.d. for Ni^{++} discharge (neglecting H_2 evolution) is $1{\cdot}6 \times 10^{-2}$

III.

Cathodic Overvoltage (volt).

Period of Decay (sec. × 10^{-3}). 0·01 amp./sq. cm.

Direct Value.	0·655	1·31	1·97	3·28	4·91	6·55	13·7	35·1	73·0	131	312	386
0·385	0·375	0·37	0·365	0·36	—	0·355	0·34	0·29	0·26	0·24	0·21	0·195
0·38	0·375	—	0·37	—	0·365	0·34	0·31	0·27	0·26	0·22	0·185	0·17
0·31	0·305	—	0·30	—	0·295	0·28	0·26	0·225	0·20	0·17	0·14	0·125
0·30	0·30	0·295	—	0·29	0·275	0·27	0·255	0·23	0·205	0·18	0·155	0·15
0·325	0·325	—	0·32	0·315	0·31	0·305	0·29	0·255	0·23	0·21	0·175	0·16
0·29	0·29	—	0·285	0·28	—	0·275	0·265	0·235	0·22	0·21	0·185	0·18
0·265	0·265	—	—	0·26	0·255	0·25	0·235	0·225	0·195	0·185	0·165	0·15
0·26	0·26	—	—	0·255	—	0·25	0·24	0·225	0·21	0·19	0·165	0·16
0·24	0·24	—	—	—	—	0·235	0·23	0·225	0·21	0·19	0·18	0·165
0·26	0·26	—	—	—	—	0·255	0·25	0·245	0·235	0·225	0·205	0·195
0·345	0·345	0·34	0·32	0·315	0·30	0·29	0·27	0·235	0·21	0·165	0·135	0·12
0·325	0·32	—	0·315	0·305	0·30	0·295	0·28	0·255	0·235	0·225	0·19	0·185
0·30	0·30	—	—	0·295	0·29	0·285	0·275	0·255	0·245	0·23	0·19	0·175
0·295	0·295	0·29	0·285	0·275	—	0·265	0·24	0·21	0·17	0·135	0·115	0·085
0·275	0·275	—	—	—	0·27	0·265	0·255	0·225	0·205	0·175	0·145	0·14
0·27	0·27	—	—	0·26	0·255	0·245	0·225	0·19	0·17	0·15	0·12	0·105

$T = 25°$.

0·335	0·335	0·33	—	0·32	0·315	0·31	0·29	0·265	0·245	0·235	0·205	0·20
0·37	0·365	—	0·36	0·355	—	0·35	0·335	0·305	0·28	0·265	0·235	0·225
0·32	0·32	0·315	—	—	0·305	0·30	0·28	0·25	0·23	0·21	0·20	0·185

0·315	0·315	0·31	—	—	—	0·30	0·29	0·28	0·25	0·23	0·22	0·195

M./20 $NiSO_4$.

0·715	—	—	—	0·71	—	0·705	0·68	0·645	0·59	0·525	0·395	0·36
0·61	—	—	—	—	—	0·61	0·56	0·46	0·41	0·37	0·28	0·26
0·54	0·53	—	—	—	0·52	0·51	0·48	0·445	0·395	0·36	0·31	0·30
0·54	—	—	—	—	—	0·53	0·52	0·49	0·46	0·42	0·315	0·28

amp./sq. cm. in M./2 $NiSO_4$ calculated from the expression $\dfrac{knFc}{d(1 - t_{Ni^{++}})}$, if the following values for the terms are assumed: $k = 10^{-6}$ g. ion/sq. cm./sec., $n = 2$, $F = 10^5$, $c = 0{\cdot}0005$ g. ion/cc., $d = 0{\cdot}05$ cm., and $t_{Ni^{++}} = 0{\cdot}37$.† If, on the other hand, the values (η_K, Table IV) of η immediately

* Agar and Bowden, *Proc. Roy. Soc. A*, 1938, **169**, 206.
† Zitek and McDonald, *Trans. Electrochem. Soc.*, 1946, **89**, 279.

after the initial rapid decay had ceased were used for η_0 at 10^{-1} amp./sq. cm., the graphs were straight lines over the whole c.d. range except

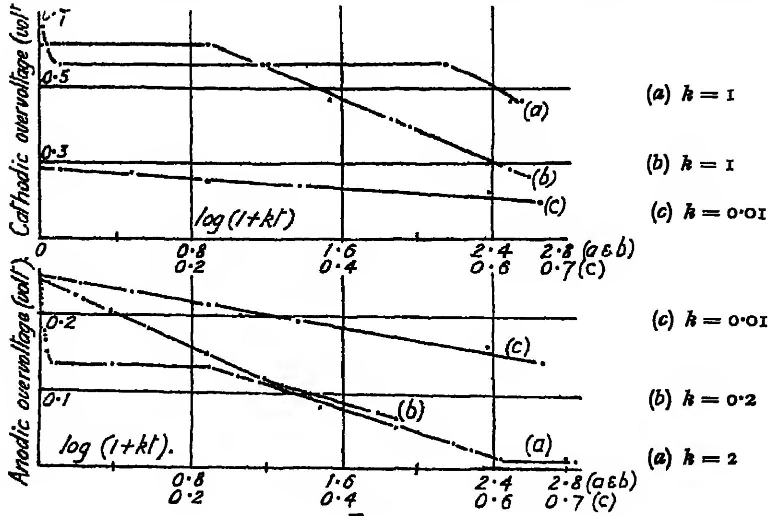

FIG. 3.

(a) $= 10^{-1}$, (b) $= 10^{-2}$, (c) $= 10^{-3}$ amp./sq. cm. t in 10^{-4} sec.

pH 2·3 and 6·7, for which η_K was respectively 0·01 and 0·06 v. too *low*.

As the c.d. is raised the rate of decay at the shorter periods is increased, and to maintain the fit of the log $(1 + Kt)$ function, K must be made larger—usually in direct proportion to the c.d.

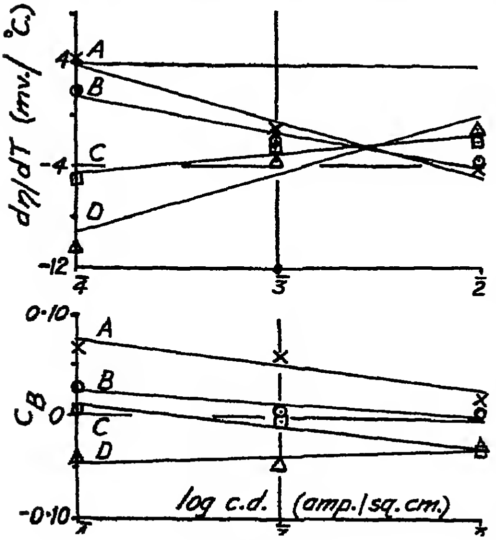

FIG. 4.

A: pH 5·5 (30°). C: pH 6·5 (30°).
B: pH 4·4 (30°). D: pH 5·5 (40°).

Effect of Temperature.—According to the c.d., an increase of temperature may raise or lower the overvoltage in a given electrolyte. In the same electrolyte $d\eta/dT$ may be positive or negative, depending upon the temperature. At a given c.d. and temperature $d\eta/dT$ may be positive in one electrolyte and negative in another. All these possibilities are illustrated in Fig. 4, where it will be seen that $d\eta/dT$ is an approximately linear function of log I. At a c.d. of about 3×10^{-3} amp./sq. cm., $d\eta/dT$ has a value of $-0·0024$ v./°c. which is apparently independent of the electrolyte and temperature.

The temperature coefficient $c_B = (B_2 - B_1)/B_1(T_2 - T_1)$ of the slope of the decay graphs for 10^{-4}, 10^{-3}, and 10^{-2} amp./sq. cm. is also an approxi-

mately linear function of log I with the electrolytes on which the effect of temperature was studied. In calculating c_B for 10^{-4} amp./sq. cm., the following values of B, which are not given in Table IV, were used: pH 4·4 (35°) = 0·101, (25°) = 0·079; pH 5·5 (25°) = 0·083, (35°) = 0·135, (45°) = 0·093; pH 6·5 (25°) = 0·035, (35°) = 0·037: the function used was $\eta_t = \eta_0 - B \log (1 + 0{\cdot}001t)$ throughout.

TABLE IV.

pH	0·0001 amp./sq. cm.	0·001 amp./sq. cm.			0·01 amp./sq. cm.				0·1 amp./sq. cm.			Static Cath. Potl. (−ve).	
	η_0.	η_0.	B.	$d\eta/dt$.	η_0.	B.	K.	$d\eta/dt$.	B.	η_K.	t_L.		b.
2·1	—	0·27	—	—	0·380	0·096	0·2	70	—	—	—	0·21	—
2·5	0·155	0·265	—	—	0·381	0·108	0·2	78·4	—	0·38	140	0·18	0·112
3·1	0·16	0·26	—	—	0·311	0·095	0·2	69	0·085	0·295	100	0·25	—
4·4	0·14	0·221	0·120	5·15	0·303	0·084	0·2	61	0·082	0·35	2·5	0·295	0·081
5·5	0·195	0·251	0·136	5·85	0·327	0·104	—	41·1	0·059	0·40	5·5	0·30	0·065
6·2	0·10	0·192	0·079	3·4	0·291	0·075	—	30	0·105	0·37	30	0·32	0·095
6·7	0·06	0·160	0·072	3·1	0·267	0·071	—	28	—	0·30	316	0·37	0·103
7·2	0·07	0·150	0·056	2·4	0·263	0·063	—	25	0·035	0·34	30	0·39	0·094
7·9	0·06	0·141	0·045	1·9	0·241	0·051	0·05	11	0·038	0·345	20	0·41	0·094
8·9	0·085	0·156	0·045	1·9	0·261	0·044	0·05	9·1	0·030	0·42	5·3	0·425	—
5·6	0·22	0·251	0·162*	13·8	0·359	0·103	0·5	149	0·105	0·44	3·5	0·29	—
5·9	0·085	0·205	0·085	3·7	0·324	0·076	0·2	55	0·090	0·44	2·2	0·295	0·120
6·5	0·07	0·181	0·070	3·0	0·302	0·067	—	27	0·097	0·425	12	0·29	0·115
7·0	0·15	0·201	0·150*	12·7	0·300	0·108	0·2	78·4	0·092	0·40	4	0·32	—
7·6	0·125	0·191	0·179	7·70	0·278	0·115	0·05	24	0·050	0·385	2·2	0·37	—
5·8	0·105	0·186	0·119	5·12	0·272	0·107	—	42·3	—	—	—	0·30	0·083
4·4	0·12	0·240	0·113	4·86	0·338	0·081	0·2	59	—	—	—	0·29	0·11
5·6	0·15	0·261	0·095	3·7	0·367	0·090	—	36	0·083	0·48	4·6	0·30	0·108
6·8	0·12	0·206	0·072	3·1	0·321	0·100	—	39·5	0·095	0·46	3·5	0·335	—
5·4	0·09	0·215	0·069	3·0	0·316	0·073	—	29	0·093	0·42	3·0	0.26	0·11
M./20 $NiSO_4$.													
2·5	0·18	0·305	0·144*	12·2	0·713	0·515	0·01	22·2	—	—	—	0·23	—
5·7	0·215	0·285	0·132	5·67	0·61	0·206	1·0	—	—	0·56	140	0·29	—
6·5	0·16	0·274	0·058*	5·0	0·529	0·197	0·05	40·8	0·29	0·61	80	0·31	—
8·8	0·18	0·226	0·100†	2·16	0·540	0·372	0·01	16·0	0·28	0·54	80	0·41	—

* K = 0·02. † K = 0·005.

For the pH 4·4 and 5·5 solutions the slope b of the $\eta - \log I$ graphs is less at 35° than at 25°, but the decrease is not proportional to the absolute temperature. At 45° the slope for pH 5·5 has increased again to its value at 25°.

Effect of Nickel-Ion Activity.—In all the M./20 $NiSO_4$ electrolytes, concentration polarisation, as shown by the upward curvature of the $\eta - \log I$ graphs, sets in just above 10^{-3} amp./sq. cm.; and this prevents direct comparison of the values of η at any higher c.d. for M./2 and M./20

solutions. Furthermore, buffering agents do not give an electrolyte of the same pH with M./20 as they do with M./2 $NiSO_4$. Comparison of results at 10^{-3} amp./sq. cm., however, between electrolytes having nearly the same buffering agents (pH 2·5, 2·1; 5·7, 5·6; 6·5, 5·6; 8·8, 7·0) suggests that the overvoltage is about 0·03 v. higher in the M./20 solutions. Owing, presumably, to reduction of $a_{Ni^{++}}$ by complex formation, the static cathode potential (Table IV) in the M./2 $NiSO_4$ electrolytes at 35° becomes, particularly with acetate buffers, more negative above pH 6·5; for most electrolytes between pH 4·4 and 6·5 it is 0·30 $\pm$ 0·01 v.* It may be mentioned that the addition of the appropriate static cathode potential (volts, H_2 scale) enables the η values at all c.d. to be converted to cathode potentials; e.g., the overvoltage of 0·16 v. at 0·001 amp./sq. cm. (pH 6·7) corresponds to a cathode potential of $-0{\cdot}16 - 0{\cdot}37 = -0{\cdot}53$ v. (H_2 scale).

Effect of pH and Buffering Agents.—At 10^{-4}, 10^{-3}, and 10^{-2} amp./sq. cm. the $\eta - p$H graphs for M./2 $NiSO_4$ electrolytes buffered with NH_4OAc at 35° have minima at approximately the following pH values: 7·0, 7·8, 7·9. With $(NH_4)_2SO_4$ buffers, the graphs for 10^{-4} and 10^{-2} amp./sq. cm. only have minima; they are at pH 6·3 and 6·5. Above pH 6·3 the overvoltage at 10^{-2} amp./sq. cm. in the NH_4OAc buffer becomes less (eventually by about 0·05 v.) than that in the $(NH_4)_2SO_4$ buffer at

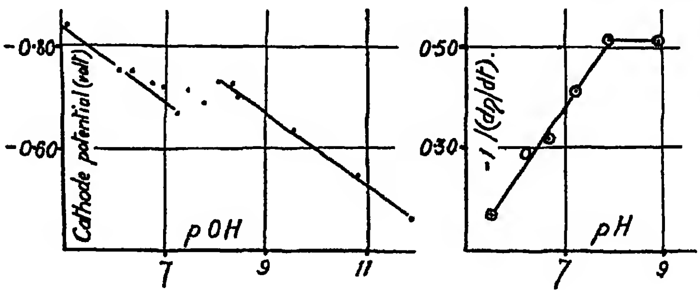

FIG. 5.

equal pH; the cathode potentials are approximately equal. At 10^{-3} amp./sq. cm., $-1/d\eta/dt$ for the M./2 $NiSO_4$ electrolytes (35°) buffered with NH_4OAc rises linearly (Fig. 5) with pH until this is 7·9, and then becomes constant. There is apparently no simple relationship between $d\eta/dt$ and pH for the $(NH_4)_2SO_4$ buffer at 10^{-3} amp./sq. cm., or for either buffer at 10^{-2} amp./sq. cm. At equal pH, $-d\eta/dt$ for the M./2 $NiSO_4$ solutions buffered with $(NH_4)_2SO_4$ is usually greater than it is for those buffered with NH_4OAc.

A very marked influence of pH and buffering agents is apparent in the behaviour of the decay of cathodic polarisation at 10^{-1} amp./sq. cm. The electrolytes of pH 6·7 and 6·5 buffered, respectively, with NH_4OAc and $(NH_4)_2SO_4$, have by far the longest duration, t_L, of halt in their groups. It is possibly significant that the buffer capacity of these electrolytes is at, or near, the maximum in each group, so making them the most effective in preventing a rise in pH at the cathode. The formation of $Ni(OH)_2$ as a colloid, or as a fine precipitate, will occur only in a thin, compact layer on the cathode surface, in contrast to a more diffuse layer such as would be produced in a poor buffer by a region gradually decreasing in pH (outwards) for a greater distance. This dense layer of $Ni(OH)_2$ may hinder diffusion and thus delay the decay of concentration polarisation. An alternative explanation of the halt is that a Ni/NiO, $n H_2O$ electrode is formed, and a

* Calculation of the potential of a Ni electrode in M./2 $NiSO_4$ at 35° using the value 0·063 for the mean activity coefficient (Harned and Owen, *Physical Chemistry of Electrolytes*, p. 427), and $-0{\cdot}25$ v. for the standard potential at 25°, gives $E_{Ni}(35°) = -0{\cdot}31$ v.

TABLE V.

pH.	Buffering Agents.	c.d. (amp./sq. cm.).	M./2 $NiCl_2$—Anodic overvoltage (volt).														
			Direct Value.	Period of Decay.													
	$T = 35°$.			0·318	0·665	1·45	2·71	6·98	14·0	31·9	69·8	110	377	779	1390	3160	3540 (sec. $\times 10^{-5}$).
5·5	M./6 NH_4Cl + M./6 NH_4OH	10^{-1}	0·40	0·21	0·17	0·17	—	0·17	—	0·17	0·13	0·085	0·06	0·04	0·025	0·005	0·00
6·4			0·26	0·15	0·135	0·135	—	0·135	—	0·13	0·11	0·075	0·05	0·03	0·01	0·01	0·005
				0·655	1·31	1·97	3·28	4·91	6·55	13·7	35·1	73·0	131	312	380		(sec. $\times 10^{-4}$).
5·5	M./6 NH_4Cl + M./6 NH_4OH	10^{-2}	0·28	0·275	0·265	0·255	0·24	0·23	0·22	0·185	0·145	0·115	0·095	0·07	0·05		
6·4			0·245	0·24	0·235	0·23	0·22	—	0·205	0·18	0·145	0·115	0·095	0·07	0·06		
				0·605	2·80	6·05	12·6	32·6	67·4	83·6	121	294	360				(sec. $\times 10^{-4}$).
5·5	M./6 NH_4Cl + M./6 NH_4OH	10^{-3}	0·24	0·24	0·235	0·23	0·22	0·205	0·18	0·17	0·16	0·13	0·11				
6·4			0·25	0·25	—	0·245	0·24	0·23	0·21	0·20	0·19	0·155	0·135				
5·5	M./6 NH_4Cl + M./6 NH_4OH	10^{-4}	0·19	0·19	—	0·19	—	—	—	—	0·185	0·16	0·155				
6·4			0·20	0·20	—	—	—	—	—	—	0·195	0·185	0·18				

constant potential is maintained until the NiO is removed by dissolution. Thus from Fig. 5 it will be seen that, over part of the range, the cathode *potential* during the halt is a linear function of *p*OH; but the slope (0·074) is greater than the theoretical value of 0·06 v. A further property of the halt is that $\eta_0 - \eta_K$ is a maximum at *p*H 6·7 for the NH_4OAc, and at *p*H 6·5 for the $(NH_4)_2SO_4$ buffers.

(b) Anodic Polarisation.—Values of η^+ at intervals throughout its decay at 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4} amp./sq. cm. in M./2 $NiCl_2$ and in M./2 $NiCl_2$ + M/6 NH_4Cl + M./6 NH_4OH are given in Table V. As with the cathodic polarisation, the course of the decay was defined by the relation $\eta_t = \eta_0 - B \log (1 + Kt)$. A value for B at 10^{-1} amp./sq. cm. in the *p*H 5·5 electrolyte is not given in Table VI, because the logarithmic portion consisted of two straight lines of different slopes. As will be seen from Fig. 3, the decay graphs for the *p*H 6·4 electrolyte are, throughout, in reverse order vertically to that which would be anticipated from their c.d. In the plain M./2 $NiCl_2$ solution the 10^{-1} amp./sq. cm. graph lies below those for 10^{-2} and 10^{-3} amp./sq. cm., but the two latter are in normal order. Both the 10^{-1} amp. decay graphs have halts lasting $3·5 \times 10^{-4}$ sec. It is possible that the Ni anode becomes semi-passive at this c.d., and an Ni_2O_3, or NiO_2, layer is formed which preserves a constant potential until it is dissolved by the electrolyte. If the rapid initial decay at 10^{-1} amp./sq. cm.

TABLE VI.

*p*H.	0·001 amp./sq. cm.				0·01 amp./sq. cm.				0·1 amp./sq. cm.			Static Anode Potl. (+ ve.).
	η_0.	*B*.	*K*.	$d\eta/dt$.	η_0.	*B*.	*K*.	$d\eta/dt$.	*D*.	η_K.	t_L.	
5·5	0·239	0·157	0·02	13·3	0·286	0·109	0·5	158	—	0·17	3·5	0·00
6·4	0·250	0·171	—	7·36	0·246	0·112	0·2	81·3	0·080*	0·135	3·5	0·04

is included, η_0 for the *p*H 6·4 electrolyte is almost independent of c.d; but if it is omitted, η^+ is 0·115 v. lower at 10^{-1} than at 10^{-2} amp./sq. cm. The $\eta - \log I$ graph for *p*H 5·5 is linear up to 10^{-2} amp./sq. cm. and has a slope of 0·045. The very high $-d\eta/dt$ values for this electrolyte are approximately equal to the highest observed in the cathodic polarisation, viz. at *p*H 5·6 (M./2 $NiSO_4$, 35°). With the *p*H 6·4 solution $d\eta/dt$ is about three times that for the cathodic polarisation at the same c.d.

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Acknowledgement is due to the Chief Scientist, Ministry of Supply, for permission to publish.

Summary.

1. At 10^{-4}, 10^{-3}, and 10^{-2} amp./sq. cm. the course of the decay of cathodic and anodic polarisation at a nickel electrode in electrolytes of widely varying *p*H and composition is defined by the relation $\eta_t = \eta_0 - B \log (1 + Kt)$. At 10^{-1} amp./sq. cm. the decay is characterised by an extremely rapid fall during the first 2×10^{-6} sec., followed by a halt lasting for $3 - 300 \times 10^{-4}$ sec., depending upon the electrolyte. The decay then becomes logarithmic and the above relation applies. With anodic overvoltage the graph for 10^{-1} amp./sq. cm. lies below those for 10^{-2} and 10^{-3} amp./sq. cm.

2. For many electrolytes the cathodic overvoltage varies with c.d. from 10^{-4} to 10^{-2}, and possibly to 10^{-1} amp./sq. cm. according to the equation $\eta = a + b \log I$, where b ranges from 0·06 to 0·12. In a *p*H 6·4 electrolyte the anodic overvoltage is almost independent of c.d.

3. For the cathodic overvoltage, $d\eta/dT$ and the temperature coefficient of B are approximately linear functions of $\log I$. They also vary with temperature and the electrolyte.

4. The cathodic overvoltage for M./2 $NiSO_4$ solutions (35°) is a minimum at certain values of *p*H which depend on the buffering agents and the c.d. Above *p*H 6·3 the overvoltage at 10^{-3} amp./sq. cm. is less in the NH_4OAc than in the $(NH_4)_2SO_4$ solutions. At 10^{-3} amp./sq. cm., $-\dfrac{1}{d\eta/dt}$ for NH_4OAc solutions increases directly with *p*H from 5·5-7·9. The duration of the halt in the decay of cathodic overvoltage is a maximum in NH_4OAc solutions at *p*H 6·7 and in $(NH_4)_2SO_4$ solutions at *p*H 6·5. The cathode potential during the halt is a linear function of *p*H from 2-5·5 and from 6·7-9.

Résumé.

A 10^{-1}, 10^{-3} et 10^{-2} amp./cm.^{2}, le survoltage, dans le dépôt ou la dissolution du nickel, décroit avec la température, d'après la relation suivante : $\eta_t = \eta_0 - B \log (1 + Kt)$. A 10^{-1} amp./cm.^{2}, la diminution est extrêmement rapide pendant les premiers 2×10^{-5} sec., puis s'arrête pendant 3 à 390×10^{-4} sec. selon l'électrolyte. La durée de cet arrêt est maximum dans des solutions de $NiSO_4$ M./2, tamponnées à *p*H 6·5 et 6·7 respectivement avec $(NH_4)_2SO_4$ et NH_4OAc. L'équation de Tafel est suivie par de nombreux électrolytes. Pour le survoltage cathodique, $d\eta/dT$ et le coefficient de température de B varient avec la densité de courant, la température et l'électrolyte. Les courbes du survoltage cathodique en fonction du *p*H montrent des minima. A 10^{-3} amp./cm.^{2}, pour des solutions de $NiSO_4$ M./2, tamponnées avec NH_4OAc, $\dfrac{1}{d\eta/dt}$ croît directement avec le *p*H de 5·5 à 7·9.

Zusammenfassung.

Bei Stromdichten von 10^{-4}, 10^{-3} und 10^{-2} A/cm.^{2} nimmt die Überspannung der Nickelabscheidung und -auflösung der Relation

$$\eta_t = \eta_0 - B \log (1 + kt)$$

gemäss ab. Bei 10^{-1} A/cm.^{2} ist die Abnahme während der ersten 2×10^{-5} Sekunden äusserst rasch, worauf eine Arrestperiode von $3\text{-}300 \times 10^{-4}$ Sekunden folgt. Die Dauer des Arrests (mit M./2 $NiSO_4$-lösungen) hat ein Maximum, bei *p*H 6·5 mit $(NH_4)_2SO_4$ und bei 6·7 mit NH_4OAc als Puffer. In vielen Elektrolyten wird Tafel's Gleichung befolgt. Bei der kathodischen Überspannung hängen $d\eta/dT$ und dB/dT von der Stromdichte, der Temperatur und dem Elektrolyt ab. Die Kathodenüberspannungs—*p*H—Kurven besitzen Minima. Bei 10^{-3} A/cm.^{2} für M./2 $NiSO_4$-lösungen mit NH_4OAc—Puffer zwischen *p*H 5·5 und 7·9 wächst $\dfrac{1}{d\eta/dt}$ direkt mit dem *p*H-Wert an.

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POLARISATION IN THE ELECTRODEPOSITION OF METALS.

By G. E. Gardam.

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The cathodic polarisation of a metal deposition process, i.e., the difference between the potential of the growing cathode and its equilibrium potential in the same solution, is caused by one or more of the processes necessary to bring the hydrated and possibly complex metal ion to the cathode, add an electron to it and build the resulting atom into one of the grains comprising the cathode deposit. The extent to which each of these may affect polarisation is discussed below using published and some new data.

1. Supply of Ions to the Cathode.

A. Concentration of Polarisation.—Although ions removed by discharge are replenished by electrolytic migration, movement of solution and diffusion, as a first approximation, the latter only is important. The polarisation resulting from the consequent concentration difference may be calculated.

The quantity of deposit per day per sq. cm. at a current density d amp. per sq. cm. is

$$\frac{d}{96{,}500} \times 24 \times 60 \times 60 = 0{\cdot}895d \text{ equivalents.}$$

This is brought to the cathode across a diffusion layer l cm. thick, the concentration adjacent to the cathode being C_2 and in the bulk of the solution C equivalents respectively. Then

$$0{\cdot}895d = \frac{D}{l}(C - C_2),$$

where D is the coefficient of diffusion of the ion, i.e., the g. equivalent diffusing across 1 sq. cm. per day per unit of concentration. D and l are constant in any one case whence

$$d = k_1(C - C_2), \text{ or } C_2 = C - \frac{d}{k_1} \qquad . \quad . \quad . \quad (1)$$

The resulting potential difference of the cathode from its equilibrium value is therefore

$$\Delta e = \frac{0{\cdot}058}{n} \log_{10} \frac{C_2}{C} = \frac{0{\cdot}058}{n} \log_{10} \left(1 - \frac{d}{k_1 C}\right) \qquad . \quad . \quad (2a)$$

and the cathode potential

$$e_c = e + \frac{0{\cdot}058}{n} \log_{10} \left(1 - \frac{d}{k_1 C}\right) \qquad . \quad . \quad . \quad (2)$$

B. Decomposition of Complex or Hydrated Ions.—The speed of dissociation of complex or hydrated ions may be a cause of polarisation. For example in silver deposition from potassium silver cyanide solution the speed of the reaction $AgCN . CN^- \rightleftharpoons Ag^+ + 2CN^-$ may be a controlling factor. Under static conditions the reaction proceeds equally swiftly in each direction, i.e.,

$$k_1[AgCN . CN^-] = k'[Ag^+][CN^-]^2 = k[Ag^+],$$

[1] Glasstone, *Trans. Amer. Electrochem. Soc.*, 1931, **59**, 277.
[2] Pugh, *J. Chem. Soc.*, 1937, 1824.

since with excess of potassium cyanide present, the cyanide ion concentration is constant.

During electrolysis at current density d and Faraday equivalent F, silver ions will be removed by deposition at rate d/F and will accordingly fall in concentration to $\{[Ag^+] - x\}$. The rate of production will be the same as the rate of deposition, i.e.,

$$\begin{aligned}\frac{d}{F} &= K_1[AgCN \,.\, CN^-] - k\{[Ag^+] - x\} \\ &= k[Ag^+] - k\{[Ag^+] - x\} \\ &= kx.\end{aligned}$$

The cathode potential will become as a result

$$\begin{aligned}e_c &= e + \frac{0{\cdot}058}{n} \log_{10} \frac{\{[Ag^+] - x\}}{[Ag^+]} \\ &= e + \frac{0{\cdot}058}{n} \log_{10} \left(1 - \frac{x}{[Ag^+]}\right) \\ &= e + \frac{0{\cdot}058}{n} \log_{10} \left(1 - \frac{d}{k[Ag^+]}\right). \quad . \quad . \quad . \quad (3)\end{aligned}$$

C. Passage of Ions through Films and other Obstructions.—The diffusion or migration of ions toward the cathode may be hindered by obstructions such as (i) porous, semipermeable or impermeable films, (ii) congregation of undischargeable cations, (iii) chemical conditions which remove a proportion of the dischargeable cation before it reaches the cathode. Colloidal substances will slowly diffuse and may migrate towards the cathode and there cause obstruction and hinder ionic movement. The precipitation in the cathode film of compounds, especially of a basic or hydroxide nature, may involve a more or less transitory colloidal phase with similar results. Such a case is well established for nickel deposition [4, 20] it is probable for all iron group metals, for chromium, manganese and similar easily hydrolysed metals.

Where an electrolyte contains several species of cations, in general only the most electropositive is discharged. The others will, however, migrate toward the cathode and may form an obstruction until removed by association. The addition of acid or of alkali metal salts is frequently used in technical electrolysis to increase conductivity but also to increase polarisation. A typical case is the addition of large quantities of sodium sulphate to a nickel depositing solution, Macnaughtan and Hothersall [3] found this to increase the polarisation greatly. Simultaneous discharge of metal and hydrogen ions, as in nickel deposition, may reduce the acidity in the diffusion layer with consequent precipitation of basic compounds and reduction of the effective ionic concentration. There is considerable reason to suppose [4] that nickel is never deposited except from a solution almost denuded of nickel ions in this way. It seems possible that the high polarisation of nickel deposition and of other iron-group metals arises in this way.

2. Discharge of Ions on the Cathode.

A. Lateral Movement of Ions.—Where the cathode is a liquid metal, the metallic atom can be accommodated wherever ionic discharge occurs; but on a solid metal either the ion is discharged where it approaches, and then awaits incorporation in the lattice, or it must move with a lateral component toward, and be discharged at, a convenient point in the growing lattice. The lateral movement of an ion through the solution would require an extra force (polarisation) which would be, as a first approximation,

[3] Macnaughtan and Hothersall, *Trans. Faraday Soc.*, 1928, **24**, 387.
[4] Macnaughtan, Gardam and Hammond, *ibid.*, 1933, **29**, 729.

directly proportional to the current density. Erdey Gruz and Volmer [5] observed that growth proceeds only on certain constantly progressing active fronts and that the current-polarisation curves were linear, at low current densities. Hoekstra [6] maintained the number of active points large and constant by continuous scraping of the cathode. He also obtained linear curves, less steep than when scraping was not used. Thon [7] indeed believes that physical union of the ion and electron is not necessary but discharge occurs where the electron lattice field is strongest, i.e., at the edge of an uncompleted atom layer. It is concluded that on solid metals a lateral movement of ions is necessary for discharge, the necessary driving force appearing as a polarisation.

B. Hindrance to the Discharge of Ions.—Contact of the free ion may not be sufficient for immediate discharge. An assumption of this nature has been fruitful in explaining the theory of hydrogen overvoltage. It has been reviewed by Glasstone [13] and discussed by Bowden,[8] Baars,[9] Brandes,[10] Volmer [11] and Gurney.[12]

Volmer [14] considers that hindrance to discharge of ions is an important factor in the deposition of the iron metals, but is more reserved about other metals. The prevalence of the logarithmic type of polarisation curve and its similarity to the hydrogen discharge curve may lend support to this view but is probably not justified.

3. Disposal of Discharged Ions.

A. Placing of Atoms in an Existing Lattice.—Examination of the microstructure of many electrodeposits reveals well defined individual grains, each presumably of a continuous lattice. Indeed, as shown by Hothersall [15] this lattice may extend that of the basis metal (this is visible in Fig. 7 and 8). By X-ray or electron diffraction, other, finer grained, deposits may be proved crystalline. Unless there is obstruction to growth of pre-existing crystals, only slight, if any, supersaturation of atoms will be necessary to proceed with an incomplete layer; a higher supersaturation will be necessary to start a new layer and a much higher supersaturation to start a new lattice or grain. A mathematical consideration [16] has led to relationship for the three cases of the form

$$e \propto d, \quad e \propto \frac{1}{\log d}, \quad e \propto \frac{1}{\sqrt{\log d}}.$$

Erdey Gruz [18] has obtained polarisation curves corresponding with the first and second of these expressions and he, with Volmer [17] also found that a cathode of carbon required a very high polarisation to commence mercury or bismuth deposition owing to the necessity of forming nuclei but that this rapidly fell once deposition started. Thus formation of new grains is unlikely to occur unless obstruction prevents continuation of the existing lattices.

[5] Erdey Gruz and Volmer, *Z. physic. Chem.*, 1931, **157**, 165.
[6] Hoekstra, *Rec. Trav. Chim.*, 1931, **50**, 339.
[7] Thon, *L'Electrolyse et la Polarisation Electrolytique* (Hermann, Paris, 1934).
[8] Bowden and Rideal, *Proc. Roy. Soc. A.*, 1928, **120**, 59.
[9] Bears, *Sitz. Ges. Beford Naturw. Marburg*, 1928, **63**, 213.
[10] Brandes, *Z. physik. Chem. A.*, 1929, **142**, 97.
[11] Volmer, *Z. physik. Chem.*, 1930, **150**, 203.
[12] Gurney, *Proc. Roy. Soc. A.*, 1931, **134**, 137.
[13] Glasstone, *The Electrochemistry of Solutions* (2nd edn., Methuen, London, 1937).
[14] Volmer, *Physik. Z.*, 1933, **4**, 346.
[15] Hothersall, *Trans. Faraday Soc.*, 1935, **31**, 1242.
[16] Erdey Gruz and Volmer, *Z. physik. Chem.*, 1931, **157**, 165.
[17] *Ibid.*, p. 182.
[18] Erdey Gruz, *Z. physik. Chem.*, 1935, **172**, 157.

B. Obstruction of Crystal Growth by Absorbed or Co-deposited Non-metallic Matter.—The production of smooth, compact and fine-grained metallic deposits is essential in technical electrodeposition; this is frequently achieved by the presence of small quantities of " addition agents ". These are diverse in character, but many are colloids which are preferentially adsorbed by metals, e.g., gelatin. Their action is no doubt to prevent, by adsorption on the metal or by cataphoretic migration, the continued growth of an existing grain and hence compel the formation of a new one. Indeed it has been shown by Wernick [19] that the efficiency of such addition agents in reducing the grain size of silver deposits, is broadly proportional to their power of protecting colliodal silver sols from flocculation by electrolytes.

Similar results may, however, result automatically without such additions. For example, the fine grain size of nickel electrodeposits has been shown [4, 20] to be due to the formation in the diffusion layer of colloidal nickel compounds and their co-deposition with the metal, restraining its grain size.

Similar evidence is available to explain the very fine grain size in chromium deposited from chromic acid solution [21, 22] and deposits from some double cyanide solutions.

Experimental.

Current density-cathode potential curves have been determined for deposition of (i) mercury from solutions of mercurous nitrate or perchlorate or potassium mercuricyanide of various concentrations, (ii) copper from cupric sulphate solutions with different sulphuric acid additions, (iii) silver from a solution of AgCN 35 g., KCN 37 g., K_2CO_3 38 g. per litre, (iv) nickel from a solution of $NiSO_4, 7H_2O$ 240 g., H_3BO_3 30 g., KCl 19 g. per litre, pH value 5·8 colorimetrically. In all cases the cathode potential was determined by the Luggin capillary, direct method using a calomel reference electrode.

The mercurous nitrate solution contained the minimum quantity of nitric acid to prevent hydrolysis. Mercurous perchlorate solutions were prepared by Pugh's method.[8] Mercuric potassium cyanide was prepared by dissolving mercuric oxide in potassium cyanide solution; mercurous cyanide appears to be unknown. A circular glass cup filled with mercury formed the cathode in a cell with a mercury-pool anode below. Measurement of current-potential curves of mercury deposition from strong aqueous mercurous perchlorate solutions which freeze below − 45° C. was attempted slightly above and below the freezing-point of mercury, but so far has been inconclusive due to experimental difficulties. In the deposition of the solid metals the cathode consisted of a circular sheet parallel to and equidistant from two flat anodes; electrolysis was carried out for 30 min. at a medium current density before readings were commenced.

Deposits of copper and silver about 0·04 inch thick were also built up on a cylindrical rod of the same metal for examination of the cross sectional microstructure. Nickel was also deposited on a sufficient volume of mercury for the cathode to remain fluid, clean and apparently homogeneous throughout.

Results.

Mercury.—Curves were obtained for each solution at various dilutions and were all of similar shape, typical examples being shown in Fig. 1 and 2. These were entirely consistent with equations (2) or (3); Glasstone [1]

[19] Wernick, *Trans. Faraday Soc.*, 1928, **24**, 361.
[20] Gardam and Macnaughtan, *ibid.*, 1933, **29**, 755.
[21] Kasper, *Bur. Stand. J. Res.*, 1932, **9**, 351; 1935, **14**, 693.
[22] Adcock, *J. Iron and Steel Inst.*, 1927, **115**, 369.

quotes values of $D = 1{\cdot}2$, $l = 0{\cdot}05$, whence k_1 (equation (2)) becomes 0·027. A larger numerical constant (0·058) showed better agreement with the experimental curves, probably owing to the horizontal disposition of the cathode.

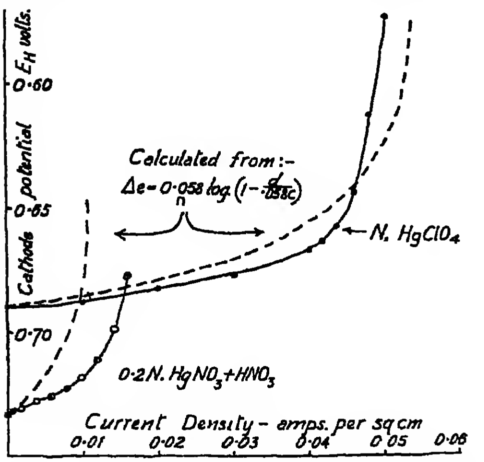

FIG. 1.—Cathode potential-current density curves for mercury deposition (full line) compared with calculated values (broken line) 20° C.

Copper and Silver.—The current-potential curves showed some or all of the following well marked divisions in sequence of increasing current density: (*a*) at very low current densities a slight rise from the equilibrium potential, (*b*) a linear portion in which polarisation and current density were directly proportional, (*c*) an abrupt discontinuity, with *increase* of $\frac{de}{dd}$, followed by a curve in which polarisation was accurately proportional to log *d*, (*d*) a rapidly increasing polarisation to the limiting current density. Typical curves are shown in Fig. 3, 4 and 5. In copper sulphate solutions, increase of temperature or decrease of acidity diminished the extent of the

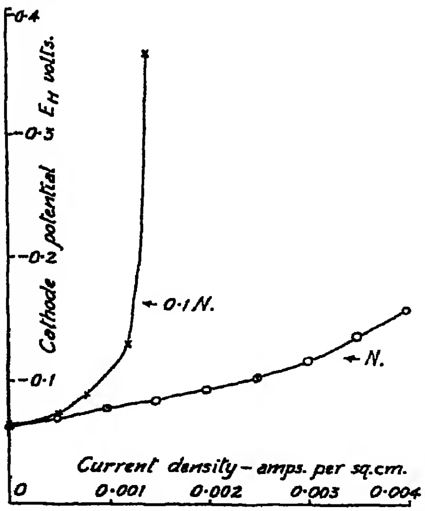

FIG. 2.—Cathode potential-current density curves for mercury deposition from potassium mercuric cyanide solution (20 C.°).

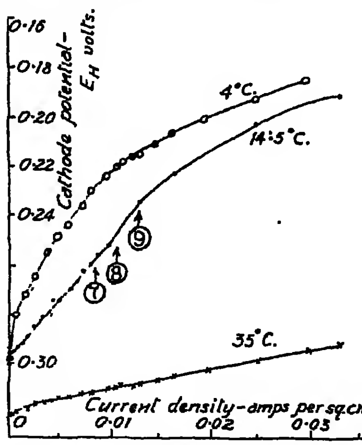

FIG. 3.—Cathode potential-current density curves for copper deposition from a solution of $CuSO_4$, $5H_2O$ 200, H_2SO_4 50 g./l. at various temperatures. The ringed numbers refer to later figures showing the microstructure of the deposit.

logarithmic portion *c*, till at 35° C., or without added acid, it was not realised. In silver potassium cyanide solutions all portions were realised, but the influence of temperature was similar.

The microstructure of numerous copper deposits showed that those prepared at current densities corresponding to section *b* were coarsely

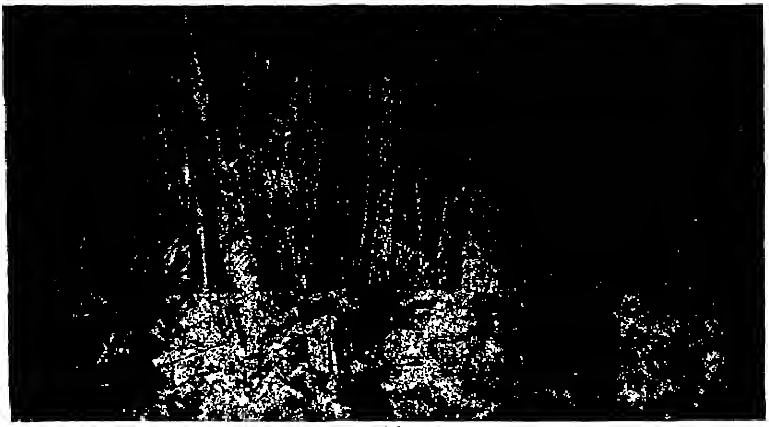

FIG. 7.—0·0088 amp./sq. cm.

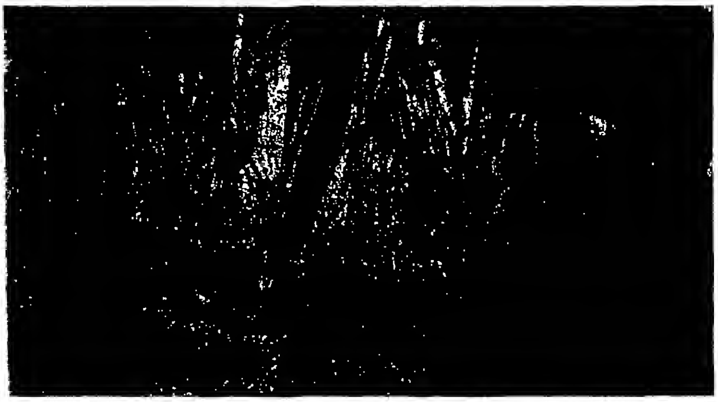

FIG. 8.—0·011 amp./sq. cm.

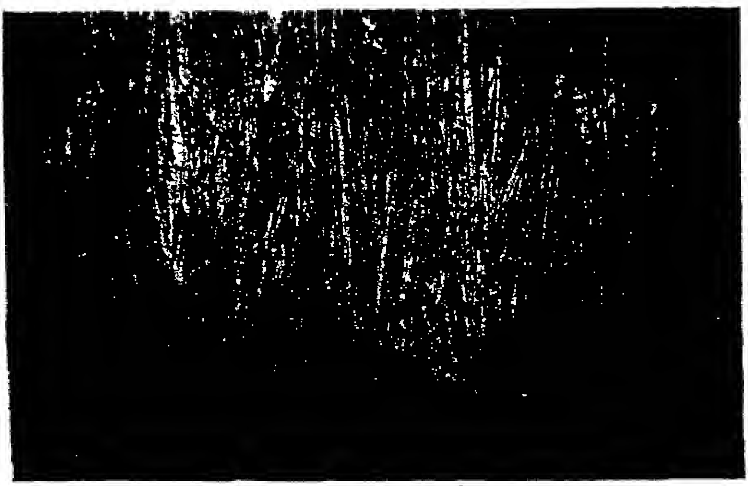

FIG. 9.—0·0132 amp./sq. cm.

FIG. 7, 8 and 9.—Microstructure of electrodeposits from $CuSO_4 . 5H_2O$, 200 g. l., H_2SO_4 50 g. l., 16° C. at current density shown, × 100.

[To face page 187

crystalline, the number of grains per unit cathode area tending to decrease with time; on section c the deposits were finer, acicular and confused, the grains per unit area remaining constant or increasing. At current densities near the transition $b - c$ twinning of the grains was observed. One typical example of each case is shown in Fig. 7, 8 and 9. The microstructure of all the silver deposits consisted of a very fine and not clearly resolvable structure; no especial distinction could be made even after annealing.

Nickel. — The current-potential curves for deposition on both solid and liquid cathodes were fairly accurately logarithmic at all current densities, and are shown in Fig. 6. The actual polarisation was, however, 0·25–0·5 v. greater on the mercury cathode. The microstructure of the solid metal was fine grained and acicular.

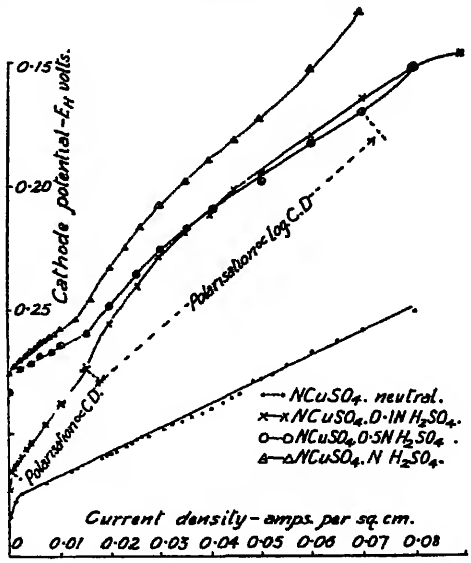

FIG. 4. — Cathode potential-current density curves for copper deposition from various sulphate solutions (20° c.).

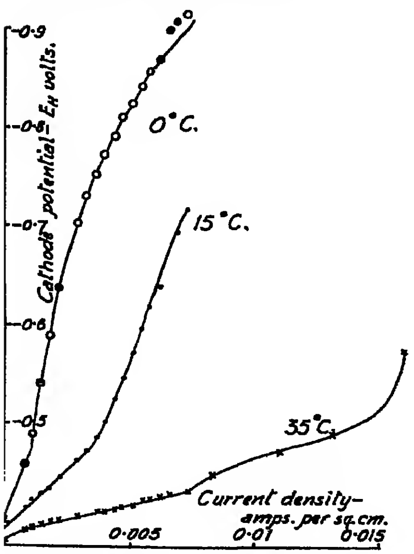

FIG. 5.—Cathode potential-current density curves for silver deposition from potassium silver cyanide solution at various temperatures.

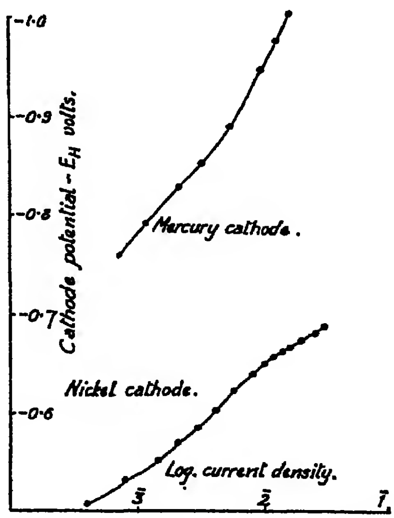

FIG. 6. — Cathode potential-current density curves for nickel deposition (20° c.).

Discussion.

The current-potential curves for deposition of liquid mercury are similar for simple and complex solutions. They are consistent with equations

(2) or (3) respectively; in the case of complex solutions, however, since the polarisation is not markedly greater than for simple solutions, there appears no justification for doubting that concentration polarisation is the chief factor operating when a liquid metal is deposited.

The very different form of the curve for nickel deposition on a mercury cathode, and in particular the high polarisation found, taking into account the high hydrogen overvoltage of mercury, suggests that difficulties of concentration polarisation and crystallisation are here negligible, and that some factor associated with hydrogen ion discharge is operative. In view of the well-known irreversibility of deposition of nickel the observation may be important. It may arise directly from the dependence of nickel ion discharge on hydrogen ion discharge or indirectly owing to the necessity of forming a high p_H cathode film from which much of the nickel is precipitated as basic material.

The current-potential curves for copper deposition from simple acid sulphate solutions and for silver deposition from complex cyanide solutions are similar to each other but more complex than the foregoing type. Only the linear current-polarisation relation at low current densities, and the logarithmic relation at high densities need be discussed here. The structure of copper deposits suggests that formation of new grain nuclei is absent in the former but common in the latter case; similar evidence was not obtained for silver possibly because of a different factor restraining grain size. The type of curve obtained for silver solution, which undoubtedly contains complex ions, was not, however, of the form given by equation (3), and it is concluded that speed of decomposition of complex ions is not the controlling factor.

Although both linear and logarithmic polarisation curves have been recorded (see ref. [26] for review), the sequence of parts does not seem to have been emphasised. Chiout [23] showed that the structure of a single copper crystal was continued by deposition of copper under conditions known from the present work to result in a linear relation, but gave polycrystalline results under other conditions. Erdey Gruz and Frankl [24] failed to continue growth of single crystals, which is surprising in view of their success with copper and silver in more complex solutions and the linear curves they obtained. Boulach,[25] using rotating cathodes in acid copper sulphate solutions, obtained very similar results to those recorded here, but owing to paucity of determinations at the lower current densities, he failed to observe the sharp discontinuity. He proposed an empirical equation of the form $C = \frac{RT}{nF}(1 + Ad^2)$ which gives a smooth curve without the sharp discontinuity.

It is concluded that the linear relation is an indication of the building up of existing grains. This seems almost certain for copper and very probable for silver. The logarithmic type is most probably a sign of frequent formation of new grain nuclei. The sudden sharp increase of $\frac{de}{dd}$ at the critical current density is less easy to understand and may result from exhaustion, in the vicinity of the cathode, of special highly activated ions, e.g., unhydrated ions; or from the accumulation of some obstruction, e.g., undischargeable hydrogen ions as suggested by Boulach.[25] The subsequent reduction of polarisation at higher current densities below the extrapolated linear graph is consistant with Erdey Gruz and Volmer's equations [16] for production of new nuclei, and the resultant increase in active centres.

It is concluded that the physical form of the cathode metal deposit may

[23] Chiout, Abstract in *Inst. Metals*, 1928, 39, 595.
[24] Erdey Gruz and Frankl, *Z. physik. Chem.*, 1937, 178, 266.
[25] Boulach, *Trans. Amer. Electrochem. Soc.*, 1938, 74, 399.
[26] Gardam, *Trans. Faraday Soc.*, 1938, 34, 698.

influence the polarisation to an extent not sufficiently appreciated and may overshadow purely electrochemical effects.

Acknowledgement is made to the Chief Scientist, Ministry of Supply, for permission to publish this paper, which describes work done at Woolwich Polytechnic, London, S.E. 18.

Summary.

The factors affecting polarisation in the electrodeposition of metals have been discussed. It has been shown that concentration polarisation or slow dissociation of complex or hydrated ions can be expressed by a formula :—

$$\Delta e = 0{\cdot}058/n \log (1 - d/kC).$$

Polarisation may also arise from passage of ions through films or other obstructions, by difficulties of discharge of ions either generally or at the required position on a solid metal, and by difficulties of disposing of the new atoms in an existing or new grain lattice. The obstruction to crystal growth by absorbed or co-deposited non-metallic matter may further increase the polarisation.

It is experimentally shown that deposition of liquid mercury from simple or complex solutions results in concentration polarisation only. In the electrodeposition of solid copper from simple, or of silver from complex solutions or of nickel, concentration polarisation is overshadowed and the relations are complex and multiple. These probably result from physical state of the deposited metal rather than from the electro-chemical conditions. The linear current-polarisation relation often found at medium current densities results from a deposit of large or increasing grain size whilst the more frequent logarithmic relation is an indication of the frequent production of new grains. The polarisation of nickel deposition on liquid mercury is considerably higher than that of deposition of the solid metal ; this is related to hydrogen overvoltage and a probable interrelation between hydrogen and nickel ion discharge.

Résumé.

On décrit ici les facteurs qui affectent la polarisation dans le dépôt électrolytique des métaux. Il est possible d'exprimer la polarisation par concentration ou la dissociation lente d'ions complexes ou hydratés par une équation logarithmique ; cependant la polarisation peut avoir d'autres causes : obstacle au passage des ions, difficultés de décharge ou de disposition des nouveaux atomes, ce qui est accru par une adsorption ou un dépôt simultané de substance non métallique, ou si la croissance des cristaux se trouve empêchée. On montre que le dépôt de mercure liquide résulte de la polarisation par concentration, mais ceci est dissimulé par des phénomènes plus compliqués pour Cu (à partir de solutions simples) et Ag (à partir de solutions complexes) où l'état physique du métal déposé affecte les résultats. La courbe courant-polarisation (pour des densités de courant moyennes) est une droite lorsqu'il s'agit de grains de grande taille, tandis que la production fréquente de nouveaux grains est indiquée par la relation logarithmique. La polarisation de Ni sur Hg liquide est discutée en fonction du survoltage d'hydrogène.

Zusammenfassung.

Die verschiedenen Faktoren, die die Polarisation bei der elektrolytischen Abscheidung von Metallen beeinflussen, werden besprochen. Konzentrationspolarisation oder langsame Dissoziation eines komplexen oder hydratierten Ions können durch eine logarithmische Gleichung ausgedrückt werden. Polarisation kann aber auch durch den Durchgang von Ionen durch Hindernisse oder durch Schwierigkeiten bei der Entladung oder bei

der Anordnung der neuen Atome verursacht werden; Schwierigkeiten, welche durch Behinderung des Kristallwuchses durch Adsorption oder Mitabscheidung von nichtmetallischen Substanzen vergrössert werden. Es wird experimentell gezeigt, dass die Abscheidung von Quecksilber nur von Konzentrationspolarisation begleitet ist, während diese im Falle der Abscheidung von Cu aus einfachen Kupfersalzlösungen oder von Ag aus Komplexsalzlösungen durch kompliziertere Vorgänge in den Schatten gestellt wird. In diesen Fällen beeinflusst der physikalische Zustand des abgeschiedenen Metalls die Resultate. Die geradlinige Stromstärke-Polarisationskurve für mittlere Stromdichten ist bei einer Abscheidung in grossen Körnern zu erwarten, während eine logarithmische Beziehung auf die häufige Erzeugung von neuen Körnern hindeutet. Die Polarisation von Ni an flüssigem Hg wird mit Bezug auf die Waserstoffüberspannung besprochen.

(a) *GENERAL DISCUSSION* *

Prof. A. R. Ubbelohde (*Belfast*) said: With regard to the remarks by Dr. Hothersall, a problem of considerable interest for the deposition of metals on electrodes, and also for the over-potential associated with such deposition, is the state of strain of the first few atomic layers and one metal on a substrate of different lattice spacing. Can it be said that if the lattice spacing of the substrate is greater than that of the deposit the first few layers will be in a state of strain, and if the lattice-spacing of the substrate is smaller the first few layers of the deposit will tend to buckle? The mechanical processes in the first few layers of a deposit will presumably be quite different from those in deposits thick enough to have reached the normal lattice spacing of the deposited metal. In particular, the mechanism of rupture of a metal under strain may be expected to be very different in thin layers, from the "normal" process in layers of appreciable thickness. It may be that thin layers will show rupture-limits approximating to the theoretical values for a lattice free from flaws; in this case the overpotential due to strain may be quite appreciable.

A cognate problem is the "stripping" of thin deposits of metal. For example, when copper is plated electrolytically on to glass the surface which has been rendered conducting, either by baking on a layer of colloidal graphite, or by depositing platinum from an organic solution, it is found to strip much more easily from Pyrex than from soda glass. Is this due to the spacing of the substrate, or to the role of hydrogen ions in producing layers in a state of strain?

Dr. G. E. Gardam (*Woolwich*) said: The generalised conclusion (eqn. (9)) of Hoar and Agar's paper, that the current distribution ratio on two independent cathodes, is the ratio of their respective anode-cathode distances, each increased by a quantity χ, is of great practical utility, since the additive factor is independent of the particular anode-cathode arrangement and is a measure only of the throwing ability of the solution. The additive factor is the product of the conductivity of the solution and a factor representative of the change of cathode potential with c.d.; if, as is frequently the case, the cathode potential-c.d. curve is such that it can be expressed by an equation, the derivative can be used in χ; otherwise the authors' equation cannot readily be used for numerical calculation.

In the practical case where the anode-cathode paths are common over most of the distance, the independent portions are relatively short and the influence of the additive factor may be predominant. Practical electro-depositors are frequently astonished at the apparently extreme throwing power observed in small fissures although the electro-deposition

* On the six preceding papers.

process is known to have only moderate throwing power on a larger scale: the explanation is clear from the authors' conclusion and the similar equations in the writer's paper.[1]

Prof. A. J. Allmand (*London*) said: Dr. Gardam suggests as one cause of overpotential in metal deposition the "difficulties of disposing of the new atoms in an existing or new grain lattice." Evidence pointing to related phenomena has been obtained in the work on electrolytic brass deposition from cyanide solution, carried out by Dr. T. Banerjee in the King's College laboratories. Working at room temperature, with a total Cu + Zn concentration of 0·5 g.-atom/l. and with the OH′ and the free CN′ concentrations essentially the same in every case, he has shown that brass of any required composition can be deposited by suitable variation of (*a*) the Cu/Zn ratio in the electrolyte and (*b*) the cathode potential. Moreover, in the main experiments, the deposits contain, without exception, either one pure phase or a mixture of two adjacent phases. Attention will be directed to three specific points.

(1) The phase-composition limits of the alloys correspond by no means exactly to equilibrium conditions, as deduced from the thermal diagram at 200° C. The existence ranges of α-, η- and ϵ-brasses, in particular the last, are definitely enlarged, whilst that of the complex γ-phase is reduced.

(2) At low cathodic polarisations, ϵ- and (ϵ +) γ-phases are preferentially deposited over a wide range of Cu/Zn ratio in the electrolyte. Using a particular appropriate Cu/Zn value, ϵ- or (ϵ +) γ-alloys are, in this case, deposited with but slight changes in composition over a very considerable cathode potential range. Hydrogen overpotential on brass cathodes exhibits a minimum in this composition region (Thompson).

(3) The relative reluctance with which the γ-phase is apparently formed is paralleled by certain further observations: (*a*) difficulty in controlling cathode potential fluctuations when depositing γ- or ($\beta + \gamma$-) alloys; (*b*) evidence that rapid changes are taking place in the deposit during (visible colour fluctuations on the cathode), or immediately after its formation (in two cases a very rapid rise in the alloy potential from a base to a more noble value, during the few minutes after completion of the electrolysis); (*c*) the formation, in certain experiments, of alloys with 24-25 % Cu, which proved to be ϵ- with a trace of η-, which would have been ($\epsilon + \beta$-) if in equilibrium, and which only developed the γ-structure after annealing.

This last observation is reminiscent of the behaviour of electrolytic manganese, which has a face-centred tetragonal structure when deposited, and which slowly changes into the form stable at room temperature, with a γ-like structure, when allowed to stand.

Dr. T. P. Hoar (*Cambridge*) said: The change of reversible potential of a metal due to stresses in it, just mentioned by Ubbelohde, may readily be calculated (by equating mechanical and electrical work) as quite small, or the order of 1 mv. or less, at any rate for metal in bulk.

$-\kappa \cdot \dfrac{\Delta E_e}{\Delta i} = \chi$, in the formula given by Agar and myself for the current ratio in the Haring cell, is, as Gardam suggests, a general measure of the throwing power of a *solution*; it is unfortunately not a constant (unless the $E_e - i$ curve is rectilinear), and can only be used to describe the throwing power of a solution over a given range of cathodic c.d.

Gardam points out that a small depression in a cathode fills up equally well in a large as in a small electroplating bath; since the current paths up to the depression and to points near to it are common, the important dimension in such a case is not the total distance between anode and cathode, but is a length of the same order of magnitude as the depth of the depression, independent of the size of the bath. In general, cathodes of equal size will receive equally well-thrown deposits in small or large

[1] Gardam, *Trans. Faraday Soc.*, 1938, **34**, 698.

baths; but if the size of the cathode is proportional to the size of the bath, a large cathode will receive a less well-thrown deposit than a small. Also, a number of small cathodes, well spaced in a large bath, will receive better-thrown deposits than one large one of equal area; but if the small cathodes are bunched together, the deposits will become less well thrown.

The Haring cell is an idealisation, in which current paths 10 and 50 cm. long to the two cathodes are deliberately kept separate; it thus gives a very conservative estimate of throwing power, quantitatively applicable only to such cases as the throwing of deposits into the interior of, for instance, tubes having dimensions near to those of the cell.

Dr. M. Haissinsky (*Paris*) said: In addition to the methods quoted by the authors, the advances realised recently in the preparation of sensitive photo-plates permit one to utilise another powerful method, i.e. photo-radioactive, for the investigation of the structures of electrolytic deposits. Let a radioelement, or a common element containing some traces of a radioactive isotope, be formed on an electrode and applied to a specially prepared photographic plate. The α- or β-rays emitted during the decay of the radioelement cause a blackening at the points where the desintegration of the atoms takes place. As illustration of the possibilities of this method three reproductions of such plates (Ilford Half-Tone concentrated) obtained with Po deposits are given in Fig. 1-3. The experimental conditions were as follows.

(1) Spontaneous deposit on a silver sheet in 10 c.c. of 0·3 N. HNO_3 containing about 1×10^{-10} g. of Po; the deposited amount is $1{\cdot}7 \times 10^{-11}$ g. and time of exposure of the plate 1 hour. The magnification is 700. As one can see, the distribution of the deposit is very uniform.

(2) Cathodic deposit on gold in nitric acid of the same normality as before, obtained at a potential very near to the critical one, i.e. just favourable to the beginning of the deposit. The initial concentration of Po was $8{\cdot}5 \times 10^{-10}$ g. in 10 cc. and time of exposure ½ hr. The deposit is here visibly concentrated in a few spots.

(3) The conditions were the same as in (2) but the Po concentration was 5 times larger; a part of the deposit was dissolved anodically. In addition to the concentrated spots, one can see an important distribution over the whole of the electrode surface. Similar plates were obtained with ThC, the isotope of Bi. These experiments, carried out in collaboration with Mrs. Faraggi and Mr. Coche, are only in their very beginning and we are not yet able to state the exact conditions that will enable us to obtain the one or the other deposit structure. In particular, it is still too early to ascertain whether the spots correspond to microscopic irregularities in the structure of the substrate or to active centres, as I have postulated in order to explain the kinetics of deposition of some radioelements.[3]

Under the conditions described, the deposit is far from being sufficient in order to cover the electrode with a monoatomic layer. We have thus the possibility of investigating the very initial stage of deposit formation. If the radioelement is used as tracer added to more important quantities of a common element (for instance ThC to Bi), the method of course permits the study of growth and further modifications of the deposit structure. It is to be noted that even in the case of the above experiments the polonium is used as its own tracer, since during the exposition only about 1/5000th or 1/3000th part of the deposit has decayed.

With reference to Gardam's paper, in the particular case of silver cyanide complex ions it is very difficult to admit that the cathode potential is dependent on the decomposition reaction postulated by the author:

$$[Ag(CN)_2]^- = Ag^+ + 2CN^-.$$

Haber has shown already in 1906 that if one assumes the potential to be defined by this reaction, the rate of the decomposition must be so

[3] *J. Chim. Physique*, 1933, **30**, 119; 1946, **43**, 21.

high that it has no physical meaning. The question was discussed later by many other authors, more recently by Glasstone [3] and by Glazunov,[4] and some other mechanisms, such as the discharge of positive complexes ions $[Ag_2CN]^+$, were suggested.

Dr. M. Haissinsky (*Paris*) (*communicated*) : New experiments realised by this method show that the spots of the Fig. 2-3 are in relation with the formation in *solution* of some colloidal hydrolytic compounds of Po (by aging). It seems that the micelles are deposited on the cathode more rapidly than the Po-ions. The investigation is continued.

Dr. H. Wilman (*London*) said : Several speakers have indicated their appreciation of the complexity of the processes and the large number of factors involved in electro-deposition. In our paper on crystal growth at the cathode we have established by electron diffraction the crystal structure, orientation, shape and degree of twinning in thin deposits or the surface regions of thick layers made under a wide range of conditions, and we have found that these facts lead to a concordant picture of the relative importance of many factors which influence growth of electro deposits.

The main primary factors which determine the actual growth of the deposits from the discharge of the cations and addition of the atoms to the substrate or deposit crystal surfaces, do in fact appear to be (1) the rate of arrival and discharge of the ions at the cathode, (2) their mobility over the cathode surface, (3) the atomic arrangement in the substrate crystal surfaces, (4) the tendency of deposition to be concentrated most on the projecting parts of the cathode surface, which is never atomically smooth on solid cathodes, and (5) the extent and nature of the adsorption or co-deposition of other ions, atoms, molecules and colloids. The main secondary factors (i) electrolyte concentrations, (ii) temperature, (iii) c.d., (iv) degree of stirring and convection, are also found to have, in general, the effects on the above primary factors to be expected from current knowledge of the structure of the deposits obtained under different conditions by (*a*) sublimation in vacuum and (*b*) crystal growth from solution.

In particular, the electron diffraction observations show clearly the very drastic hindrance to crystal growth and the resulting random disposition of the deposit crystals, when a hydrogen overpotential is present, i.e. hydrogen is deposited but not evolved. They show further the important effect of the mobility of the ions or atoms over the cathode surface (until they reach positions of lowest potential energy there) in tending to cause preferential growth of crystals with the most closely-packed plane parallel to the substrate. Anyone who has looked down a microscope and seen the Brownian movements of colloidal particles can hardly fail to appreciate that the vigorous impacts of the solution molecules on the cathode must result in considerable movement of the ions and atoms near or deposited on the cathode surface; and the similar effect of the thermal vibrations of the atoms about their mean positions in the crystal lattice at the cathode surface is also clearly shown by the electron diffraction observations that sublimed metal deposits are amorphous on substrates cooled in liquid air but crystalline at room temperature. The tendency for electro-deposition on projections is well known (dendritic structures) but the results described here illustrate the circumstances under which this becomes so prominent as to impose its characteristic crystal orientation against that favoured by lateral mobility. It is hardly necessary to emphasise the effect of the substrate crystal lattice on the deposit crystal orientation, since this is now well appreciated, but two slides [5] will help to convey the sort of picture one visualises of random and

[3] *J. Chem. Soc.*, 1929, 690.
[4] *Z. physik. Chem.*, 1939, 185, 393.
[5] Finch and Whitmore, *Trans. Faraday Soc.*, 1938, 34, 640, Fig. 1 and 3.

orientated deposits crystals (in this case, of ionic type) on amorphous and on crystalline substrates respectively.

The microphotographs of nickel on brass shown by a previous speaker are very interesting as illustrations of the way in which deposition may be concentrated not only on projections, but in other conditions conversely at the bottoms of depressions so as to fill them up rapidly and produce a level surface in a layer about as thick (0·005 in.) as the depression was deep and broad. Such a filling-in of depressions may perhaps result if hydrogen is deposited and adsorbed on the main-level cathode surface nearest the anode, but less so in the depressions, where metal ions could therefore be neutralised and deposited more rapidly. The deposits shown in these photographs seem to have a very fine grain structure which would support this explanation.

An example where the intercrystalline boundary depressions caused by etching a copper substrate had not been appreciably filled in though the nickel deposit was much thicker than their average width ($\sim$ 20,000 A.) is shown by some slides from previous published results.[6] In this case the microphotographs showed that the deposit surface was practically parallel to that of the substrate, faithfully repeating all the irregularities at the substrate crystal boundaries.

Mr. L. Yang (*London*) said: While various theories have been put forward for the explanation of the hydrogen overvoltage, our paper is specially concerned with the effect produced by this suppressed evolution of hydrogen on the growth of the deposited metal crystals. In our paper it has been pointed out that, for metals of high hydrogen overvoltage (i) the deposit consists of randomly disposed crystals, or even of amorphous structure, when deposited under conditions such that the evolution of hydrogen is completely suppressed by the hydrogen overvoltage, (ii) with other conditions unchanged, by raising the c.d. (provided this does not make the deposit spongy or tree-like) until hydrogen evolves continuously, the deposited metal crystals are orientated. This observation may be considered as a direct evidence which shows that before the evolution there is something accumulated on the cathode surface, which interferes with the growth of the deposited metal crystals, although it is not possible to say definitely whether the accumulated substance is hydrogen atom or hydrogen ion.

With regard to metal overvoltage, the results in our paper have shown that when the cathodic polarisation is high, the most-densely-packed lattice-plane orientation of the deposited metal crystals is not observed owing to the low mobility of the metal ions over the cathode surface. This is in agreement with Dr. Gardam's suggestion that at least part of the cathodic polarisation may be attributed to the difficulty of the lateral movement of the metal ions over the cathode surface.

Mr. E. A. Ollard (*London*) said: Although he had not had time to read through the paper of Finch *et al.* as carefully as he would have liked, he had formed the opinion that it suggested that a thin deposit made upon a metal surface completely covered the base metal with an even layer. In point of fact, however, this was not the case. Deposits started to grow from various points on the surface. In the case of a nickel deposit made under ordinary conditions on to pickled brass it might be a minute or so before the brass surface was completely covered.

With regard to the filling-up of small cracks and imperfections on the surface, this was not a question of throwing power, but was more usually a function of the surface itself. Under the conditions described above the metal would fill a thin deep crack if it were of small dimensions, but in the case of a wider scratch of larger size, the metal deposit would follow this round, and the scratch would reproduce on the surface of the deposit.

[6] Finch and Williams, *Trans. Faraday Soc.*, 1937, 33, 564.

The exact conditions governing this phenomena were at the moment under investigation, and it was hoped to find some law governing it in due course.

Mr. A. W. Hothersall (*Woolwich*) said: The general conclusions reached by Finch, Wilman and Yang are in agreement with the picture sketched from previous results of the way in which the structure of electro-deposited metals is built up and the results help to fill in some of the detail in a useful manner. The authors' interpretation of the action of hydrogen ions or atoms in blocking the access of metal ions and so interfering with the continuation of existing lattice layers does not seem satisfactorily in accord with some results which suggest that, in certain metal deposition processes, a much greater effect is produced by basic metallic compounds precipitated at the cathode face as a result of H^+ ion discharge while in other processes, where many H^+ ions are present but none are discharged (such as copper deposition from acid sulphate solution), addition to the solution of excess of sulphuric acid or of alkali metal sulphate makes comparatively little difference to the indentation hardness of the deposit. A marked hardening of copper deposits results from addition of gelatin and one wonders whether the random orientation of the authors' Pb deposit prepared from a perchlorate solution may not have been due to the gelatin rather than to the effect of undischarged H^+ ions. It would be useful if the authors would define the term "random orientation".

Mr. L. Yang (*London*) (*communicated*): The questions raised by Mr. Hothersall on certain points in our paper are due to some misunderstandings of what we really mean.

We do not mean that hydrogen ions in the solution, which are adsorbed on the cathode surface in a more or less dynamic state, or the hydrogen atoms on the cathode surface which can combine easily to form hydrogen molecules and then evolve as gas bubbles (provided the evolution of hydrogen is not in excessive amount), would influence seriously (*a*) the continuation of the crystal lattice of the substrate by the deposit in the initial stage and (*b*) the development of crystal orientation in thick deposit. Our idea is that a strong disturbing effect on (*a*) and (*b*) is found only when the cathode potential has exceeded the discharging potential of hydrogen ions in the corresponding solution but, owing to a comparatively high hydrogen overvoltage of the deposited metal, the hydrogen ions, brought to the cathode surface by the electric field, are either adsorbed on the cathode surface in a more static manner or, after discharge, the hydrogen atoms formed accumulate on the cathode surface but are not evolved as gas. It is in this accumulated ionic or atomic state that hydrogen will seriously interfere with the growth of the deposit crystals. In the example cited by Mr. Hothersall (deposition of Cu from an acid copper sulphate bath), this situation will never be reached even if the acidity of the solution is varied within a wide but reasonable range or if alkali metal sulphate has been added to the solution. Besides, copper has a comparatively low hydrogen overvoltage. Therefore, it is not surprising that change of the acidity or the addition of alkali metal sulphate causes little influence on the growth of the copper crystals and hence their hardness.

Also we do not mean that this accumulated state of ionic or atomic hydrogen is the only disturbing factor on (*a*) and (*b*) above. We have mentioned repeatedly that colloidal substances like gelatine and co-deposited basic metal hydroxides may also modify the structure of the deposit. Although microscopic evidences have shown that they can limit the crystal size of the deposit, their influences on (*a*) and (*b*) do not seem to follow as a natural consequence. Copper deposited from an acid copper sulphate bath (200 g. $CuSO_4 . 5 H_2O$ and 30 g. H_2SO_4 per litre of solution, c.d. 0·75 amp./dm.^{2}, bath temperature 25° C.) containing 2·5 g. gelatine per litre, shows practically the same (110) orientation as copper deposited under the same conditions from the same bath except that no gelatine has been added. Nickel, as shown in our paper, deposited

on copper single crystals continues the lattice of the substrate up to 30,000 A. or more, yet the deposition of nickel has been considered as a case associated with the codeposition of basic metal hydroxides. Therefore, the effect of gelatine and basic metal hydroxides on the structure of electrodeposits, as emphasised by Mr. Hothersall, seems to be only limited to the crystal size of the deposit but negligible, if any, on the other respects of the structure of the deposit.

Mr. Hothersall has asked for the definition of the term "random orientation." I am afraid we have not used this term, composed as it is of two incompatible words, at all in our paper. The only place where this terms appears is in the Introductory paper by Mr. Hothersall.

I wish to draw attention to the importance of a careful examination of the conditions of the cathode surface before the measurement of hydrogen overvoltage. The surface of less noble metals, though of the highest purity, if left exposed even to non-contaminated air, will soon become covered with a thin layer of oxide which can be detected very easily in the electron diffraction camera. Scratching or polishing the cathode surface before use do not help much and polishing may make the matter even worse owing to the formation of an amorphous Beilby layer on the surface. I need not cite the active metals like Fe as examples, and even those comparatively inert metals like Cu, Pb and Sn are oxidised very easily. Thus, a piece of electrodeposited copper, if left exposed at room temperature to air for a few minutes, becomes covered with a thin layer of Cu_2O. Tin, though slightly longer time is required, is oxidised to SnO. Electrodeposited lead seems to be so active that a layer of PbO is formed even if the surface has been exposed to distilled water for ten seconds.

Dr. J. B. O'Sullivan (*Manchester*) (*communicated*): An extreme case of uneven crystal growth at the cathode was observed during experiments on the passage of a direct current through Cellophane impregnated with salts. Such material behaves essentially like an aqueous salt solution under electrolysis, but ionic migration and diffusion are much slower, and convection is virtually absent. In one experiment, a piece of Cellophane which had been impregnated in a 20 % solution of $AgNO_3$, and subsequently conditioned at 65 % R.H., was electrolysed between bull-dog clips lined with copper foil. Instead of silver plating on to the copper cathode, an elaborately "treed" deposit formed in the Cellophane, as shown in the illustration, which is taken from a paper shortly to be published in the *J. Text. Inst.* The conductivity of the slightly swollen gel which forms the electrolyte, was very low, namely 0·5 millimhos/cm., and the voltage gradient was high, about 50 v./cm., this being possible owing to the low conductivity of the material. These conditions of low conductivity, high potential gradient and an unstirred electrolyte, are precisely those which are known to favour "treeing", but the present case is exceptionally pronounced.

Dr. W. J. Dunning (*Bristol*) (*communicated*): Metal plating, which is being deposited electrolytically on a cathode, may or may not fill in cracks and scratches on the surface. Among the factors which may have an influence are the dimensions of the scratches and the number of scratches per unit area. This is due to the chemical potential (and hence the electrochemical potential) of the surface within the crack being lower than that of the surface, thus favouring growth of nuclei and deposition of metal within the crack and the eventual healing of it. The difference between the chemical potentials is greater the narrower the crack and the greater the number per $cm.^2$.

This is analogous to the increased vapour pressure p_r of a small liquid droplet, radius r, compared with the vapour pressure, p_∞, of a plane surface of the same liquid (Gibbs-Thomson).

$$\mu_r - \mu_\infty = RT \log \frac{pr}{p_\infty} = \frac{2\sigma}{r}$$

where σ is the surface tension.

Consider in a metal of simple cubic structure an idealised crack, the walls of which are 110 type lattice planes, its depth l_2 and length l_3. Assume that a metal atom inside the crystal has six bonds, one with each of its nearest neighbours and each bond of strength E. Following the methods of Stranski and Kaischew, the chemical potential μ_2 of the surface 2 will be smaller the smaller the value of l_2 and is approximately given by

$$\mu_{2\infty} - \mu_2 = d\left(\frac{1}{\sqrt{2}l_2} - \frac{1}{l_3}\right)E,$$

where d is the diameter of the metal atom. Putting $d = 3$ A., $E = 0{\cdot}3$ ev. and $l_3 = \infty$, the difference in chemical potentials will be 1 mv. when $l_2 = 0{\cdot}6\ \mu$. If the crack is ten times as large, the difference is only 0·1 mv. Hence the smaller the cracks the more readily they will heal.

Again, if l_1 is the average distance on the surface between cracks, the chemical potential of the surface planes (1) of the cathode is greater than that of a smooth extensive 100 plane by an amount (approximately)

$$\mu_1 - \mu_{1\infty} = d\left(\frac{1}{l_1} + \frac{1}{l_3}\right)E.$$

It will be seen that the larger the number of cracks per unit area the higher will be the chemical potential of the surface 1.

Dr. F. Wormwell (*Teddington*) said: Dr. Agar and Dr. Hoar have drawn our attention to a matter of some theoretical and practical interest,

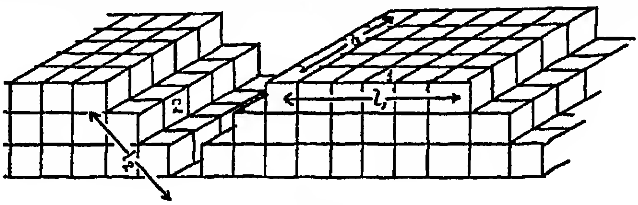

FIG. 1.

in pointing out the influence of the linear dimensions of electrochemical systems on the relative importance of electrical conductivity and of electrode polarisation. If the dangers of extrapolation from small-scale experiments to large-scale service systems are not sufficiently realised, this paper should serve to drive home the lesson.

From our work at Chemical Research Laboratory we can confirm the preponderating importance of polarisation in corrosion cells. The direct influence of electrical conductivity is usually much less than is often supposed.

In their discussion of the conditions for "true" model experiments, Dr. Agar and Dr. Hoar have rightly stressed the difficulties of adjusting the conditions in the cell to allow for polarisation effects. In natural waters such as fresh hard water or sea-water, the influence of deposits of calcium and magnesium compounds on the polarisation at cathodes is most important. Adjustment of conductivity alone may lead to appreciable errors because of the change in polarisation consequent on the reduction in concentration of the calcium and magnesium salts. I should like to ask whether some satisfactory compromise can be effected between the two extremes of using either the natural water itself or the diluted water in model experiments.

Dr. J. N. Agar (*Cambridge*) said: I agree with Dr. Wormwell that polarisation is often the predominant factor in small cells, such as those associated with corrosion, and also that "true model" conditions can be achieved without any change in the conductivity of the electrolyte, provided polarisation remains predominant over the whole range of linear dimensions under consideration. The argument developed by Hoar and

myself depends on the fact that the polarisation tends to be more important in small systems and the electrolytic resistance in large. This has not always been appreciated; one can find cases where the results of small-scale experiments have been applied to large-scale systems, regardless of the fact that the relative importance of polarisation and resistance is reversed by the change of scale.

The possible, and in some cases probable, change of polarisation characteristics with concentration of electrolyte is the greatest obstacle to the application of the "true model" technique described in our paper. Such changes can be investigated independently; as regards the film-forming solutes commonly present in natural waters, it may sometimes be possible to reduce the conductivity of the electrolyte without appreciably altering the concentration of these solutes.

Dr. V. Levich (*Moscow*) (*communicated*): I should like to point out that the exact solutions found for cases of electrodes of simple geometrical forms may be qualitatively applied to electrodes of a more complicated geometrical form too. This method gives more than a simple application of dimension analysis, which has been also discussed by D. Frank-Kamenezky.[7] In particular, this generalisation can help in choosing the numbers m and n in the formula

$$Nu = (Re)^m (Pr)^n.$$

In the case of laminar flow, n must be always equal to 1/3. The MacAdams formula cited in the report of Agar can be applied only if $Pr < 100$, but not in the case of a larger Pr (1000 and more).

Mr. A. W. Hothersall (*Woolwich*) (*communicated*): It seems curious that Salt makes no mention of hydrogen overpotential as a possible contributing factor to the overpotential observed in nickel deposition. As Gardam has pointed out in his paper, the deposition of hydrogen and of nickel are inseparably connected; and there is some experimental evidence in support of the view that the initial process in the deposition of nickel (at least from solutions below about pH 6·5) is deposition of hydrogen. Salt does not appear to have estimated the cathode efficiency in his experiments but from existing data obtained from similar solutions the following approximate results would be expected.

pH.	Overall Current Density amp./cm.².			
	10^{-2}.		10^{-3}.	
	Probable Efficiency Ni %.	Corresponding c.d. of H depn. amp./cm.².	Probable Efficiency Ni %	Corresponding c.d. of H depn. amp./cm.².
2·1	90	10^{-3}	70	3×10^{-4}
5·6	99	10^{-4}	95	$0{\cdot}5 \times 10^{-4}$

Calculation of the H overpotential corresponding to these c.d.'s of H deposition, if made on the same basis as that used by Salt to calculate his nickel overpotential (difference between static and dynamic potentials which for hydrogen could be derived from the Tafel equation) suggests that an appreciable part of the total overpotential at low pH may be due to hydrogen; indeed it is hard to avoid such a conclusion when bubbles of hydrogen can always be seen during nickel deposition. Calculation of hydrogen overpotential in buffered solutions is of course open to the objection that, since the pH at the cathode face is higher than in the bulk solution, the static potential is not known, but this objection also applies to calculation of nickel overpotential.

[7] *J. Physic. Chem.* (*Russ.*), 1945, **20**, 225.

Dr. J. T. Barker (*Flint*) said: We have had a number of special theoretical details as to particular cases of overpotential and polarisation. What I wish to bring forward is something of a more general and indeed more purely physical nature, with respect primarily to the latter. The well-known polarisation formula has two particularly important applications, to the spontaneous processes of secondary or electrolytic cells and of primary cells, working under a minimum of restraints. Taking as an example of the first, a cell with 30 % NaOH as electrolyte, graphite cathode and platinum anode, operated at 50° c. by 4 v. in the external circuit, we shall have, since the true back E.M.F. of this cell is 1·5 v.,

$$E_A + E_K + I(R_i + R_e) = \text{resultant E.M.F.} = 2{\cdot}5 \text{ v.}$$

where the first two items are the polarisations and the second two, the P.D.'s expended in the two ohmic, non-inductive resistances. Assuming a negligible change in the internal resistance, R_i, with operation, the sum of the polarisations is determined at each instant by the current. Ultimately, these will in general increase and the current will steadily fall. It is apparent also that E_A and E_K can react upon each other. If E_A is unusually high for a given current, E_K will be unusually low. The whole process is spontaneous, from the closing of the circuit.

As an example of a primary cell, we may take sodium amalgam, with an electrolyte of conc. NaOH solution and a hydrogen cathode. The polarisation formula is

$$E_A + E_K + I(R_i + R_e) = \text{driving E.M.F.} = E.$$

E will steadily diminish and E, E_A, E_K will change spontaneously and have mutual reactions. For instance, if any two of them happen to change linearly with the current, the third must do the same. E, E_A, E_K have three major spontaneous relationships, viz., those with current, quantity of electricity and time of operation. General dynamical theory indicates that polarisation is an electrical force or P.D., rising spontaneously at the surface of an electrode, in a sense like butter on milk, through the operation of deep-seated causes, definitely dynamic in character. In this connection some of the relevant dynamical ideas are to be found in the closing chapters of Clerk Maxwell's *Matter and Motion* and appendices by Sir Joseph Larmor. Practical benefits will doubtless accrue from the detection of particular agencies by piecemeal studies of electrode processes, but it is already sufficiently clear, I think, that a general theory of polarisation, of which overpotential is a part only, cannot result from such an approach. I should like to suggest that the investigation of the two types of cells I have mentioned, along the lines indicated, is a matter which is worth following up.

Dr. J. O'M. Bockris (*London*) (*communicated*): The use of sealing wax and Necol varnish described in Salt's paper seems hardly desirable as it is almost certain to introduce some poisoning effect. Nickel can easily be sealed to glass. The use of "Analar" reagents without further purification may also lead to the introduction of electrocapillary active substances into the solution.

Mr. F. W. Salt (*Swansea*) (*communicated*): In reply to Mr. Hothersall, the codeposition of nickel and hydrogen cannot be discussed with certainty on the basis of data for the separate processes, because the extent to which they influence each other is not known. If it is assumed that the separate processes are unmodified, the relation between nickel overvoltage (ηNi) and hydrogen overvoltage (ηH) at a given cathode potential, π, is given by

$$Eo_{Ni} + \eta_{Ni} = \pi = Eo_H + \eta_0 + \eta_H,$$

$$\text{or} \quad Eo_{Ni} + a + b \log I = \pi = 0{\cdot}66\, p\text{H} + a' + b' \log I'$$

where η_0 is the concentration polarisation for hydrogen evolution, and the pH is that of the cathode film. The observed overvoltage is not the

sum of the nickel and hydrogen overvoltages. In an electrolyte of $p_H > 4$ and $a_{Ni^{++}} = 1$ at 35°, the discharge of Ni^{++} will be preferential to that of H^+, and hence the cathode potential will be determined by the cathode potential—c.d. curve for Ni^{++} discharge. For $p_H < 4$ the cathode potential at low c.d. may be determined by the curve for H^+ discharge. Under static conditions the p_H, and the $[Ni^{++}]$, at the cathode face will equal that of the bulk solution. The static cathode potential is not required in the measurement of hydrogen overvoltage, which is calculated with respect to the reversible hydrogen electrode.

In reply to Dr. Bockris, disc Ni electrodes were used to minimise changes of cathode area owing to deposition of Ni, and I was unable to seal these to glass. Hydrogen overvoltage is particularly sensitive to poisons, yet the results of Coates [8] for W sealed directly into glass are within 0·01-0·02 v. of those of Hickling and Salt, who used sealing wax.

Dr. J. O'M. Bockris (*London*) (*communicated*) : With regard to the relation of metal overvoltages (at the interface M^{z+}/M) to the properties of M, it seems relevant to point out that the order of the metals arranged according to their overvoltages is roughly the converse of that according to their hydrogen overvoltages.[9] This would tend to indicate an opposite relation with the work function of the metal to that existing for hydrogen overvoltage. A simple interpretation of this fact seems to support a slow neutralisation theory of metal overvoltage.

[8] *J. Chem. Soc.*, 1945, 484.
[9] Bockris, *Nature*, 1947, **159**, 539 ; Joffé, *Uspechi. Chem.*, 1943, **12**, 438.

REACTIONS AT MERCURY CATHODES.

By J. G. Hoogland.

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In the electrolysis of sodium chloride with a mercury cathode no hydrogen is evolved but sodium amalgam is formed. This needs explanation since the reaction

$$NaCl + H_2O \longrightarrow NaOH + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2 \quad . \quad . \quad (1)$$

needs a minimum E.M.F. of 2·3 v. whereas the reaction

$$NaCl \longrightarrow Na(Hg) + \tfrac{1}{2}Cl_2 \quad . \quad . \quad . \quad . \quad (2)$$

requires 3·2 v. It may be noted that these voltages agree with the heat effects of these reactions, i.e. 52,200 cal. and 77,800 cal. resp., or 2·27 and 3·37 v., the last value requiring a correction of about 3 × 58 mv. as the concentration of the sodium amalgam is usually about 10^{-3} M. Therefore the difference between the free energy and heat effect is negligible —an assumption one is often forced to make as the temperature coefficients are seldom known.

The difference of E.M.F. (0·9 v.) between (1) and (2) is named overvoltage and is usually explained by assuming that mercury (in contrast to such metals as Pt, Fe, Ni) does not catalyse the reaction

$$2H \longrightarrow H_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus, it may be supposed that atomic hydrogen is first formed—either according to $H^{\bullet} + \ominus \longrightarrow H$, or, when primarily $Na^{\bullet}$ is discharged, according to $Na + H^{\bullet} \longrightarrow Na^{\bullet} + H$—and that H atoms subsequently combine to give molecular hydrogen.

Thus the decomposition voltage of reaction (2) should not be compared with that of (1) but with

$$NaCl + H_2O \longrightarrow NaOH + \tfrac{1}{2}Cl_2 + H \quad . \quad . \quad . \quad (4)$$

As (3) develops a heat of 98,500 cal., reaction (4) should need a supply of 101,500 cal., yielding a decomposition voltage of 4·4 v. For a true comparison it would be necessary to introduce some corrections, but even without these, it is clear that the assumption of the primary formation of atomic hydrogen may be a sufficient explanation of the occurrence of reaction (2).

Clearly, this is no proof of this assumption. Another possible explanation is the formation of hydrides, or we may imagine that the discharge of $H^•$ ions is hindered in some way at mercury cathodes. The supposition of the primary formation of atomic hydrogen, however, has the advantage that it explains in an easy manner not only all observed phenomena at mercury cathodes but also many of those observed in the dissolution of metals in acids.

Some properties of sodium amalgam which are believed to support this theory will now be discussed. As pointed out above, two reactions are possible in the electrolysing of a solution containing $Na^•$ ions, viz.,

$$Na^• + \ominus \longrightarrow Na(Hg) \text{ and } H^• + \ominus \longrightarrow H$$

but the second reaction only takes place when a catalyst for the reaction $2H \longrightarrow H_2$ is present.

Now it is well known that the potential of a sodium amalgam electrode in such a solution is a reversible one and the same holds for a hydrogen electrode at platinised platina. The last phenomenon proves, at least at this electrode material, that the discharge of $H^•$ ions takes place in a reversible manner. There is no reason to suppose that this should not be the case at mercury cathodes and by combining these facts it may be assumed that the equilibrium

$$Na(Hg) + H^• \rightleftarrows Na^• + H + Hg \quad . \quad . \quad . \quad (5)$$

is set up.

The following heat effects are known:

$$\begin{aligned} Na + H_2O &\longrightarrow NaOH + \tfrac{1}{2}H_2 + 44{,}200 \text{ cal.} \\ Na + Hg &\longrightarrow Na(Hg) \qquad + 18{,}800 \text{ cal.} \\ 2H &\longrightarrow H_2 \qquad\qquad + 98{,}500 \text{ cal.} \end{aligned}$$

which figures enable us to calculate the heat effect of reaction (5) by adding 1 mol. of OH′ ion thus changing it in:

$$Na(Hg) + H_2O \rightleftarrows NaOH + H + Hg$$

It follows that reaction (5) gives a heat effect of 23,600 cal., equivalent to a voltage of 1·03 v., in the backward direction.

However tempting it may be to manipulate these values further, e.g., to calculate the pressure of atomic hydrogen in equilibrium with sodium amalgam, etc., this can hardly be justified. The only conclusion to be drawn is that sodium amalgam should be in equilibrium with atomic hydrogen at a low, but with molecular hydrogen at a very high, pressure. This was the explanation of a phenomenon which was observed in the electrolysis of sodium chloride in mercury cells.

The so-called decomposers of these cells showed, after some time, cavities in the iron, and in cross-section these appeared to contain a combustible gas; the iron crystals were disrupted at such places, and the pressure in these cavities must therefore have reached 4×10^3 atm. at which pressure iron breaks. This is simply explained by atomic hydrogen diffusing into the iron and forming molecular hydrogen at places where there is a catalyst; the pressure of the thus formed H_2 becoming sufficiently high to give rise to these phenomena.

These and some other facts, indicating the presence of atomic hydrogen, lead to the theory outlined above that sodium amalgam in aqueous solution is in equilibrium with atomic hydrogen. As it is known that oxygen combines with atomic hydrogen according to

$$H + O = O + H \longrightarrow H\text{—}O\text{—}O\text{—}H.$$

One of the consequences of this way of representation is that, under favourable conditions, it should be possible to reduce oxygen with sodium amalgam and form peroxides.

In view of the reactivity of atomic hydrogen and peroxide, and of the observations of Baker [1] who found that H_2O_2 is reduced quantitatively by amalgam, it was expected that this reaction would take place with great difficulty. This was a fact indeed and only after many vain attempts was the formation of peroxides obtained and then, at first, with bad yields and at very low concentrations.

As an example it may be mentioned that once, when a strip of V2A-steel was immersed in mercury to test its suitability as a construction material for technical application, the yield of peroxide declined rapidly to zero, and it was impossible afterwards to attain reasonable yields. Neither cleaning of the whole apparatus with nitric acid, distillation of the mercury, nor cleaning with a concentrated alkaline solution of H_2O_2 gave any improvement. *Only after renewing the reaction liquid many times were the normal* yields attained.

Without doubt this hindrance was due to " poisoning " of the mercury and the apparatus with a very small quantity of an alloy metal, probably chromium, as it is known from experience that this metal is an extremely active catalyst in the formation of molecular hydrogen. This strongly supports the theory that the reduction of oxygen by amalgam takes place via atomic hydrogen. It is improbable that a direct reduction of oxygen by sodium to peroxide should be so very sensitive to catalysts.

It would take too long to sum up the whole course of the research so that only the results are given. The first condition for production of H_2O_2 is that the concentration of the amalgam must be very low, of the order of 0·0002 % by weight. This concentration can be measured electrochemically, e.g., against a zinc rod placed in the liquid. It was found that the voltage giving the best yield varied with the concentration of NaOH, providing that the other conditions were the same. This could be expected from a consideration of reaction (5). We may suppose, for a definite concentration of oxygen and speed of stirring, that the best yield will be attained at an equal concentration of atomic hydrogen. Now the NaOH concentration influences the voltage of the amalgam in two ways, viz., by reason of $Na^{\bullet}$ ion and $H^{\bullet}$ ion concentrations, but the zinc electrode is only influenced by the latter. Exact measurements, however, were very difficult to make and therefore this has not been pursued.

The second factor, which is important, is the oxygen concentration ; if this is high, it is possible to attain a higher concentration of H_2O_2, and to work with more concentrated amalgams. It may be imagined that two competing reactions take place at the same time, viz.,

$$O_2 + 2H \longrightarrow H_2O_2 \text{ and } H_2O_2 + 2H \longrightarrow 2H_2O.$$

and so theoretically the concentration of H_2O_2 attainable at the same yield and at the same $H^{\bullet}$ ion concentration should be proportional to the pressure of the oxygen.

In addition, other important factors are a large surface of contact between amalgam and liquid, efficient stirring of amalgam and liquid, and an absence of catalysts. Stabilisers for peroxides will obviously exert a favourable influence. Finally, concentrations up to about 3 % and at yields of 60 % were obtained with oxygen under normul pressure. At higher pressure this concentration could be increased considerably.[2]

I wish to record my appreciation and my sincere thanks to my friends, Dr. Ir. J. J. de Haas from the Royal Dutch Salt factory and Dr. Ir. J. Smittenberg from the Bataafsche Petroleum Maatschappij, who have

[1] *J. Chem. Soc.*, 1913, **103**, 2060.

[2] B.P. Application No. 1680 (1946) and U.S.A. Patent, No. 656,770 (cp. also the technical preparation of Na perborate).

performed experiments to test the ideas expressed above with so much patience and insight.

It is hoped that some elucidation of the reactions taking place at a mercury cathode has been provided and that the theory, which explains these phenomena in terms of the presence of atomic hydrogen, has been strengthened.

Summary.

Assuming that the phenomenon of overvoltage at mercury cathodes is due to the presence of atomic hydrogen, a theory is developed according to which the following equilibrium exists:

$$Na(Hg) + H^{\bullet} \rightleftarrows Na^{\bullet} + H + Hg.$$

The results of experimental work undertaken to establish that atomic hydrogen formed in this manner is able to reduce oxygen to peroxide have been outlined, which have led to a process for the manufacture of peroxide compounds from amalgam and oxygen, suited to technical production.

Résumé.

Supposant que le survoltage sur les cathodes de mercure est dû à la présence d'hydrogène atomique, l'auteur développe une théorie selon laquelle l'équilibre : $Na(Hg) + H^{\bullet} \rightleftarrows Na^{\bullet} + H + Hg$ a lieu. Le travail expérimental, entrepris pour établir que l'hydrogène atomique formé de cette manière est capable de réduire l'oxygène en peroxyde, a été esquissé et a conduit à un procédé de fabrication de composés peroxydés à partir d'amalgame et d'oxygène, procédé applicable à une production technique.

Zusammenfassung.

Ausgehend von der Annahme, dass die Überspannung an Quecksilberkathoden auf die Gegenwart von atomaren Wasserstoff zurückzuführen ist, wird eine Theorie entwickelt, derzufolge das folgende Gleichgewicht sich einstellt:

$$Na(Hg) + H^{\bullet} \rightleftarrows Na^{\bullet} + H + Hg.$$

Die Resultate der Versuche, die angestellt wurden zum Beweiss, dass der so gebildete atomäre Wasserstoff imstande ist, Sauerstoff zum Peroxyd zu reduzieren, werden umrissen. Diese Versuche haben zu einen technisch durchführbaren Prozess für die Herstellung von Peroxyden aus Amalgam und Sauerstoff geführt.

RECENT APPLICATIONS OF CONTROLLED POTENTIAL ELECTROLYSIS.

By James J. Lingane.

Received 7th February, 1947.

In applications of electrolysis for either analytical or preparative purposes the prime factor which ought to be controlled is the potential of the working electrode, since this determines the intensity of the reducing or oxidising effect, and yet the extensive literature in the field reveals that the principle is all too seldom appreciated and utilised. For example, the classical investigations of Sand,[1] Fischer,[2] Lassieur,[3] and others whose

[1] Sand, *Electrochemistry and Electrochemical Analysis* (Blackie and Son, Ltd., London and Glasgow, 1940), Vol. II.

[2] Fischer, *Z. angew. Chem.*, 1907, **20**, 134; *Z. Elektrochem.*, 1907, **13**, 469.

[3] Lassieur, *Electroanalyse Rapide* (Paris, 1923).

work has been reviewed by Böttger,[4] have amply demonstrated the great utility of the controlled potential technique in electrogravimetric determinations of metals, and yet such procedures are scarcely mentioned in most texts and reference books of analytical chemistry and electrochemistry. That these methods have not attained recognition commensurate with their merit is well illustrated by the fact that the requisite apparatus has never appeared on the market in the United States, and the analytical electrolysis apparatus purchasable to-day, although considerably more elegant in appearance, is functionally identical with that available fifty years ago.

The chief reason for the lack of enthusiasm for controlled potential methods has doubtless been that the classical manually operated circuits are tedious to operate and require constant supervision during a determination. This objection is no longer valid, because Hickling,[5] Caldwell, Parker and Diehl,[6] and Lingane,[7] have recently described circuits which automatically perform the function of maintaining the potential of a working electrode constant at any predetermined value, and thus require no attention, during the entire course of an electrolysis. With such an apparatus, for which Hickling coined the name "potentiostat," the performance of electrogravimetric determinations is just as convenient as by the much less selective "constant current" methods. Furthermore, by employing the polarographic method with the dropping mercury electrode, or with solid microelectrodes, as a pilot technique to establish optimum electrolysis conditions, various other analytical possibilities inherent in automatic controlled potential electrolysis may be exploited advantageously. This paper describes some illustrative applications of such techniques that have been made in the author's laboratory during the past few years.

Electrical Apparatus.

The potentiostat described by Hickling[5] employs vacuum tubes as control elements and thus has the advantage of being completely electronic without moving mechanical parts, but the electrolysis current is limited to that (0·3 amp.) passed by the control tubes. The circuit of Caldwell, Parker, and Diehl[6] is applicable with large currents; however, it controls in only one direction, i.e., it prevents the cathode potential from becoming more negative than a predetermined value during the course of electrolysis but it does not correct a positive drift. The apparatus devised by the author[7] controls in both directions, it is applicable with applied voltages and currents of any magnitude, its component parts are relatively easy to assemble, and it does not require preliminary calibration. The essential features of the circuit are shown in Fig. 1.

The total voltage applied to the cell is controlled by the 100 w., 30 Ω radio potentiometer rheostat R_1, which is rotated at 0·2 r.p.m. by the reversible motor M. The total applied e.m.f. is indicated by the voltmeter V_1, and the multiple range ammeter A measures the electrolysis current. The control circuit comprises a saturated calomel reference electrode S.C.E. (or any other suitable reference electrode) connected to the electrolysis cell by a salt bridge, a 100 Ω radio potentiometer rheostat R_2 powered by a 1·5 v. dry cell and set to the e.m.f. which it is desired to maintain between the working electrode and the reference electrode, a voltmeter V_2 which indicates the control potential, and a galvanometer relay G (Weston Electric Instrument Co., Model 30). Off-balance in the control circuit causes the galvanometer relay to make

[4] Böttger, *Physikalishe Methoden der Analytischen Chemie* (Akad. Verlagsgesellschaft, Leipzig, 1936), Teil II.
[5] Hickling, *Trans. Faraday Soc.*, 1942, 38, 27.
[6] Caldwell, Parker, and Diehl, *Ind. Eng. Chem.* (*Anal.*), 1944, 16, 532.
[7] Lingane, *ibid.*, 1945, 17, 332.

contact either right or left and operate one of the electronic relays Ry which control motor M. The motor then rotates R_1 at 0·2 r.p.m. until the total e.m.f. applied to the cell is increased or decreased by such an amount that the cathode potential returns to the value set on R_2, and thus the control circuit is restored to balance and the motor stops. Mechanical connection between the motor and R_1 is made by a belt drive which has the advantage of serving as a simple friction clutch so that R_1 can be moved manually if desired. The time of response between the instant when the galvanometer relay makes contact and rheostat R_1 begins to move is only a few tenths of a second. The sensitivity of the instrument depends on the sensitivity of the galvanometer relay and the resistance in the control circuit; the Weston Model 30 galvanometer relay responds to $\pm$ 15 μamp., and since the resistance in the control circuit (chiefly in the salt bridge between the reference electrode and cell) need not exceed 1000 Ω, a sensitivity of $\pm$ 0·015 v. is easily attained. This is ample for the great majority of applications of controlled potential electrolysis. For complete details of the circuit the original paper[7] should be consulted.

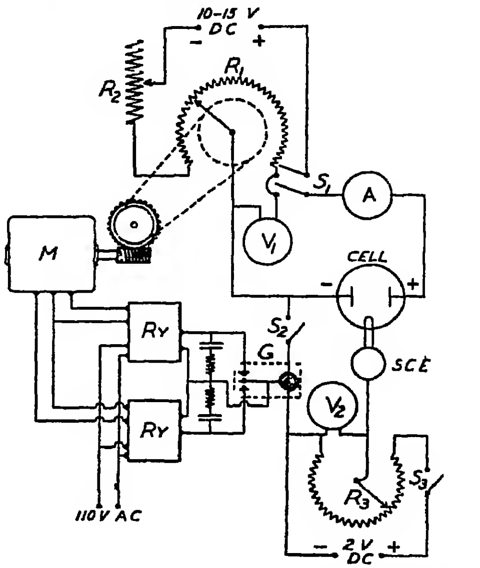


FIG. 1.—Potentiostat for controlled potential electrolysis (*Ind. Eng. Chem.* (*Anal. Ed.*), 1945, 17, 332).

Combination of Controlled Potential Electrolytic Separations and Polarographic Analysis.

In practical applications of polarography[8] to the analysis of alloys it is sometimes possible by proper choice of supporting electrolyte and the judicious use of complex-forming reagents to adjust the half-wave potential of the metal being determined to a value more positive than the half-wave potentials of the other metals present, and when this condition is satisfied it is not necessary to carry out preliminary separations. On the other hand, when the metal being determined has a fairly negative half-wave potential (e.g., Cd, Zn, etc.) and the solution contains large amounts of more easily reducible metal ions (e.g., Cu, Pb, Bi, etc.) it frequently is not possible to eliminate interferences merely by the choice of supporting electrolyte. In such cases preliminary separations are required, and controlled potential electrolysis can serve as a convenient and generally applicable means of removing the interfering metals.

In contrast to precipitation methods, electrolytic separations do not require the introduction of large amounts of extraneous reagents, which may complicate subsequent polarographic analyses, possible loss of minor constituents by coprecipitation is avoided, and when a potentiostat is

[8] Kolthoff and Lingane, *Polarographic Analysis and Voltammetry. Amperometric Titrations* (Interscience Publishers, Inc., New York, 1946).

employed separations require very little of the operator's time. It is advantageous to use a mercury cathode, rather than platinum, in order to capitalise on the fact that polarograms conveniently obtained with the dropping mercury electrode furnish all the required information concerning cathode potential and solution composition for a given separation, so that the feasibility of a proposed separation can be ascertained quickly with a minimum amount of laborious trial-and-error experimentation.

A systematic procedure for the analysis of solutions of the copper group metals, recently described in a paper from this laboratory,[8] furnishes a good example of the utility of controlled potential electrolytic separations with a mercury cathode prior to polarographic analysis. As shown in Fig. 2, polarograms of solutions containing Cu, Bi, Pb, and Cd, in a tartrate supporting electrolyte of *p*H between 3·6 and 5·5 show well separated waves of all four metals. At the optimum *p*H of 4·5 (curve *b*) all four metals can be determined simultaneously from a single polarogram

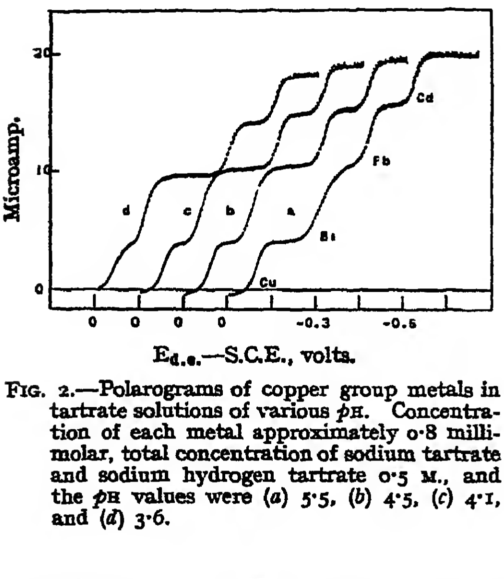


FIG. 2.—Polarograms of copper group metals in tartrate solutions of various *p*H. Concentration of each metal approximately 0·8 millimolar, total concentration of sodium tartrate and sodium hydrogen tartrate 0·5 M., and the *p*H values were (*a*) 5·5, (*b*) 4·5, (*c*) 4·1, and (*d*) 3·6.

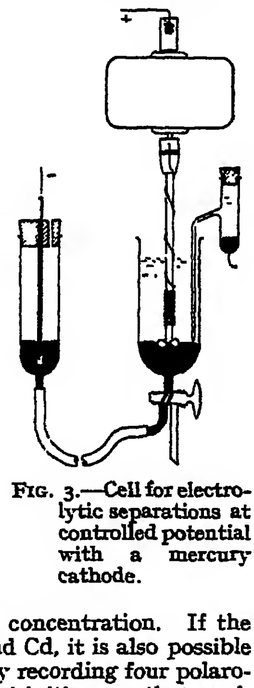


FIG. 3.—Cell for electrolytic separations at controlled potential with a mercury cathode.

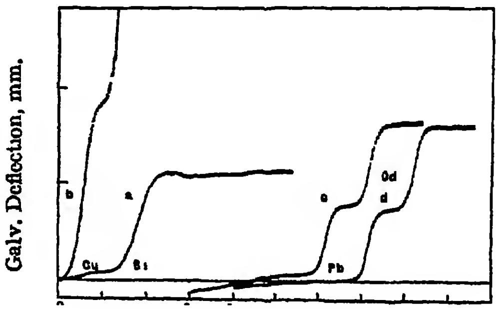
provided that they are present at about the same concentration. If the concentrations increase in the order Cu, Bi, Pb, and Cd, it is also possible to obtain a complete analysis of the group simply by recording four polarograms at successively increased galvanometer sensitivities, so that each wave in turn is magnified to a value large enough for accurate measurement of its diffusion current. However, when one of the more easily reducible members of the group predominates, so that its wave masks those of the more difficultly reducible minor constituents, preliminary removal of the interfering metal is necessary.

The cell used [8] for the separations is shown in Fig. 3; it has a capacity of about 75 cc. and the area of the mercury pool cathode is about 10 cm.[2] The mercury-solution interface is kept in rapid motion by the motor-driven glass propeller. A silver wire wrapped on the stirrer shaft serves as anode; a platinum anode is undesirable because it introduces hydrogen ion into the solution and changes its *p*H, and also because Bi tends to be oxidised and precipitated as the pentoxide on a platinum anode. The tip of the salt bridge from the saturated calomel reference electrode is

[8] Lingane, *Ind. Eng. Chem.* (*Anal.*), 1944, 16, 147.

placed very close to the electrode surface to minimise the amount of ohmic potential drop included in the apparent cathode potential. In separations at controlled potential the current is a reliable criterion of the progress of the electrolysis; it usually decreases exponentially with time and, especially with the mercury cathode, falls to a very small constant value when the electrolysis is complete. The time required is usually 30 to 45 minutes.

For separating the copper group metals the best supporting electrolyte is one containing 0·4 M. sodium tartrate, 0·1 M. sodium hydrogen tartrate, and 0·1 M. NaCl (to furnish chloride ion for the reaction at the silver anode), with a *p*H of about 4·5. In this supporting electrolyte the half-wave potentials are Cu −0·09 v., Bi −0·23 v., Pb −0·48 v., and Cd −0·64 v. against the saturated calomel electrode.[9] The optimum potential for a given separation is slightly beyond the half-wave potential of the metal to be deposited but well below the beginning of the wave of the metal to be left in solution. From curve *b* in Fig. 2 the predicted optimum potentials are: Cu-Bi, −0·15 v., Bi-Pb, −0·37 v., and Pb-Cd, −0·55 v., with a permissible variation of about ±0·03 v. in each case. The fact that in every instance satisfactory separations resulted when these potentials were employed demonstrates the reliability of the polarographic method as a pilot technique.



$E_{d.e.}$—S.C.E., volts.

FIG. 4.—Polarographic analysis of the copper group with the aid of electrolytic separations in a case where Bi predominates. (*a*) Original solution containing 1·04 millimolar Cu, 10·07 millimolar Bi, 0·400 millimolar Pb, and 0·465 millimolar Cd, in tartrate supporting electrolyte of *p*H 4·5. Galvanometer sensitivity 1·70 μa./mm. (*b*) Polarogram of solution *a* repeated with galvanometer sensitivity increased to 0·0680 μa./mm. (*c*) Solution remaining after removal of Bi (and Cu) by electrolysis with the mercury cathode at − 0·37 v. Galvanometer sensitivity 0·0680 μa./mm. (*d*) Comparison solution containing same concentrations of Pb and Cd as the original solution. Galvanometer sensitivity 0·0680 μa./mm.

The polarograms in Fig. 4 were obtained in a typical experiment with a solution that contained a large amount of Bi and small amounts of Cu, Pb, and Cd.[9] Curve *a* was recorded with the original solution. Since the copper wave is well in advance of that of bismuth, the copper can be determined easily by recording a second polarogram at an increased sensitivity of the recording galvanometer, as shown by curve *b*, but the small waves of Pb and Cd in curve *a* are completely masked by the large bismuth wave. Curve *c* was obtained after the Bi (and Cu) had been removed by electrolysis with the mercury cathode at − 0·37 v. Curve *d* is the polarogram of a comparison solution containing the same concentrations of Pb and Cd as the original solution. Comparison of curves *c* and *d* shows that no detectable amounts of Pb or Cd were lost during the removal of Bi. Equally good separations were obtained with solutions in which Cu and Pb predominated.[9]

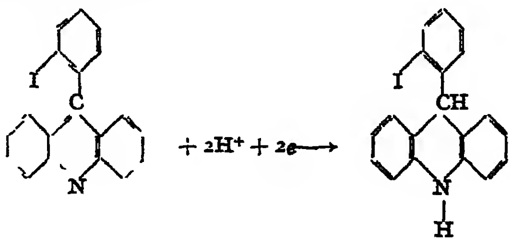
Several metals may be successively separated from the same solution without removing it from the electrolysis cell; after each separation a small sample is taken with a pipette and polarographed.

The writer has also used a platinum cathode for controlled potential separations in connection with the polarographic determination of Pb, Sn, Ni,

and Zn in copper-base alloys.[10] Two samples were used; from one of these Cu was removed prior to the polarographic determination of Pb and Sn, and from the other Cu, Pb, and Sn were removed prior to the determination of Ni and Zn. The separations were made from a dilute (0·5 M.) HCl solution; Cu was removed at − 0·35 v., and Cu, Pb, and Sn at − 0·70 v. against the S.C.E. Very satisfactory results were obtained.

Electrolytic Preparations.

Preparative electrochemistry, particularly of organic compounds, offers one of the most fruitful fields for the application of controlled potential electrolysis. The recent work of Lingane, Swain, and Fields [11] on the selective reduction of 9-(*o*-iodophenyl)-acridine to 9-(*o*-iodophenyl)-dihydroacridine according to



I. II.

furnishes a good example of the practical utility of the method, and the selectivity that can be obtained in reductions at the mercury cathode.

The problem was approached by first studying the polarographic characteristics of iodophenyl-acridine in many different supporting electrolytes. It was finally found that *o*-iodophenyl-acridine produces a double polarographic wave in a supporting electrolyte composed of 0·1 M. KOH, and 0·5 M. potassium acetate in 90 % ethanol as shown in Fig. 5.[11] The first wave corresponds to the above reaction, and the second to the reduction of the iodine in compound II to form dihydrophenylacridine. The half-wave potentials of the two waves are − 1·32 v. and − 1·62 v. against S.C.E.

With this polarographic information as a guide, preparative experiments were then carried out with the cell shown in Fig. 6. The area of the mercury cathode in the left-hand compartment was 68 $cm.^2$, and a pool of mercury in the right-hand compartment served as anode. A sintered glass disc D fused into the cross arm prevents mixing of the catholyte and anolyte. Both compartments contained the same alkaline supporting electrolyte (0·1 M. KOH and 0·5 M. potassium acetate in 90 % ethanol), and the catholyte was freed from air with a stream of nitrogen since compound II is easily air-oxidised. The preparative reductions were made with the potential of the mercury cathode at − 1·36 to − 1·39 v. against S.C.E., a value well below the half-wave potential of the second polarographic wave. After complete reduction, compound II was recovered from the catholyte by diluting with water and extracting with chloroform in an atmosphere of nitrogen.

In several experiments in which 0·8 g. quantities of compound I were reduced, compound II was obtained in a high degree of purity with an average yield of 90 %; the 10 % loss was attributed to incomplete extraction rather than incomplete reduction.[11]

This constitutes a good test case because it presents about as many

[10] Lingane, *Ind. Eng. Chem.* (*Anal.*), 1946, 18, 429.
[11] Lingane, Swain, and Fields, *J. Amer. Chem. Soc.*, 1943, 65, 1348.

difficulties as one is likely to meet; compound I is only slightly soluble in water, necessitating the use of a supporting electrolyte containing a large proportion of non-aqueous solvent, compound II is very sensitive to air-oxidation, or to anodic oxidation unless a diaphragm cell is employed and there is only a difference of 0·3 v. between the two stages of reduction. Before polarographic information was obtained, all chemical reducing agents that were tried either did not effect reduction of I or else led to the undesired complete reduction of II with elimination of iodine.

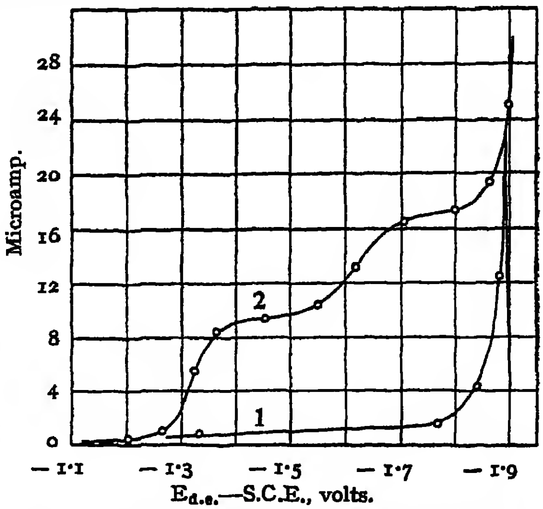


FIG. 5.—Current-voltage curve, obtained with the dropping mercury electrode, of a solution containing 2·22 millimolar *o*-iodophenylacridine in 0·1 M. KOH and 0·5 M. potassium acetate in 90 % ethanol. Curve 1 is the residual current curve of the supporting electrolyte alone.

Coulometric Analysis.

This new electroanalytical method is based on the measurement of the quantity of electricity passed during the complete reaction at an electrode of the substance being determined. The first analytical applications of this principle appear to have been made by Szebelledy and Somogyi.[12] These investigators employed *constant current* electrolysis with platinum electrodes, and electrolysed until a suitable indicator in the solution signalled completion of the desired reaction, at which point the circuit was interrupted and the quantity of electricity passed determined by means of a silver weight coulometer in series with the cell. The method of Szebelledy and Somogyi is capable of high precision, but since the electrode potentials are not controlled it is limited to cases where only one electrode reaction is possible.

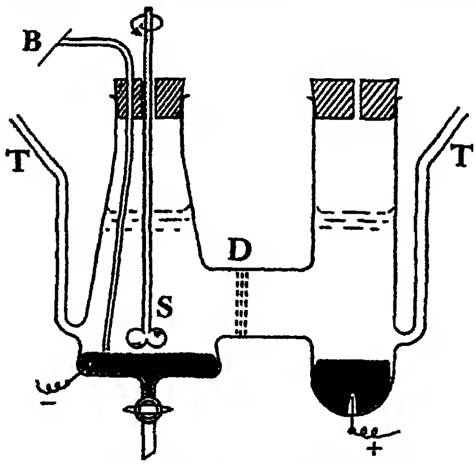


FIG. 6.—Cell for electrolytic preparations at controlled potential with a mercury cathode.

The first coulometric experiments by controlled potential electrolysis

[12] Szebelledy and Somogyi, *Z. anal. Chem.*, 1938, **112**, 313, 323, 332, 385, 391, 395, 400.

are those of Hickling,[5] who demonstrated by measurement with a hydrogen coulometer that 100 % current efficiency can be obtained during the reduction of cupric ion, and the oxidation of iodide ion, at platinum electrodes.

Because of the easy reduction of hydrogen ion on platinum, which limits the use of platinum cathodes to the determination of substances of fairly high oxidation potential, the writer recently developed a method of coulometric analysis using a mercury cathode at controlled potential.[13] The use of a mercury cathode also enables one to predict optimum electrolysis conditions from the known polarographic characteristics of the substance being determined.

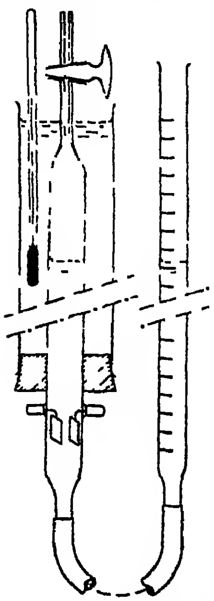


FIG. 7.—Hydrogen-oxygen coulometer for coulometric analysis. The volume of hydrogen-oxygen evolved from the platinum electrodes in the central, water-jacketed tube is measured in terms of the volume of electrolyte displaced into the adjoining buret.

The cell employed for coulometric analysis is very similar to that in Fig. 3, except that a larger (area *ca.* 80 cm.^{2}) silver wire anode is used, and provision is made for removing dissolved air from the solution with an inert gas. Removal of air is necessary because dissolved oxygen is reduced at a mercury cathode at potentials more negative than about − 0·1 v. against the S.C.E.;[8] for the same reason a platinum anode cannot be used. The quantity of electricity passed is conveniently measured by means of a hydrogen-oxygen coulometer of the type shown in Fig. 7, which has the advantage of being direct reading and furnishes a continuous indication of the progress of the electrolysis. In agreement with Lehfeldt,[14] the writer found that the hydrogen-oxygen coulometer is an accurate instrument (± 0·1 % or better) provided that pure Na or K sulphate solution, rather than the commonly recommended NaOH or H_2SO_4, is used as electrolyte.

To prepare for a coulometric determination a known volume (e.g., 100 cc.) of the supporting electrolyte alone is placed in the cell, air is removed with hydrogen or nitrogen, the potential of the mercury cathode is adjusted by the automatic potentiostat to the value to be used in the determination, and electrolysis is allowed to proceed for about 10 min. until traces of reducible impurities are removed and the current falls to a very small value (usually less than 1 ma.). The coulometer reading is then taken, and, without interrupting the circuit, a known volume (e.g. 10 to 50 cc.) of a solution of the substance to be determined is pipetted into the cell. The electrolysis is then allowed to continue under automatic control until the decrease of the current to its original very small value indicates complete reduction. The amount of substance reduced is calculated by the usual relations from the coulometer reading. Complete details are given in the original paper.[13]

Table I summarises results obtained [13] in the coulometric determination of various quantities of Cu and Bi from acidic tartrate solutions (*p*H = *ca.* 4·5), and of Pb from 0·5 M. KCl. The concentrations of the metal ions ranged from about 1 to 20 millimolar.

The accuracy of the method compares favourably with that of ordinary electrogravimetric determinations. The average error in terms of milliequivalents (± 0·01) is the same for all three metal ions, and it corresponds to ± 0·17 cc. in the coulometer reading.

[13] Lingane, *J. Amer. Chem. Soc.*, 1945, 67, 1916.
[14] Lehfeldt, *Phil. Mag.*, 1908, (6), 15, 614.

When the electrode reactions proceed with thermodynamic reversibility it is possible to achieve a high degree of selectivity in coulometric analysis with the mercury cathode. For example the half-wave potentials in the reversible reduction of Pb and Cd ions from 0·5 M. KCl (− 0·42 and − 0·62 v. against S.C.E.) differ by only 0·2 v., and yet, by electrolysing with the potential of the mercury cathode at −0·50 ± 0·02 v., it was possible to determine Pb in the presence of both larger and smaller quantities of Cd with the same accuracy as in the absence of Cd.[13] When the various reduction potentials differ sufficiently it should be feasible to successively determine several metals from the same solution by the coulometric method, and this possibility is being investigated.

In these experiments the current was found to obey the relation

$$i = i_0\, 10^{-kt},$$

where i is the current at time t, and i_0 is the initial current at the start of the electrolysis. With the particular cell used, i_0 ranged from about 30 to 300 ma. depending on the concentration of metal ion, and the current usually decreased to less than 1 ma. after 40 to 60 min. The constant k was found to be independent of the nature and concentration of the substance reduced, but it does depend on the geometry of the cell, the area of the mercury cathode, temperature, stirring rate, and similar factors. The exponential relation between current and time, which shows that complete reduction is only approached asymptotically, appears to be the chief factor which limits the accuracy of coulometric determinations.

TABLE I.—Coulometric Determination of Copper, Bismuth, and Lead.

Metal.	Quantity mg.	Solution Volume cc.	Average Error. mg.	Average Error. milliequiv.
Cu	6-74	50	± 0·3	± 0·009
Bi	13-105	50	± 0·7	± 0·010
Pb	41-207	100	± 0·9	± 0·009

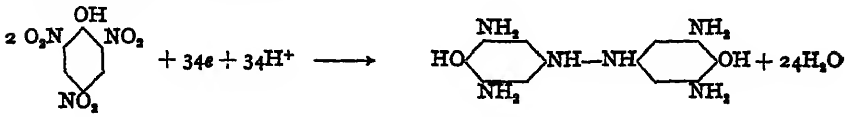
Coulometric Determination of Polarographic Reduction States.

Although the Ilkovic equation [8] can often be used to decide the reduction states corresponding to polarographic waves observed with the dropping electrode, this method becomes increasingly uncertain, and usually fails entirely, when the number of electrons per molar unit of reduction is large, because of the general lack of sufficiently accurate diffusion coefficient data. In such cases the coulometric technique with the mercury cathode may serve advantageously.

The reduction of picric acid, recently described by the writer,[18] furnishes a good illustration. From 0·1 M. HCl as supporting electrolyte the reduction of picric acid produces a well developed polarographic diffusion current between − 0·6 and − 1·5 v. against S.C.E. The unusually large value of the diffusion current constant ($i_d/Cm^{2/3}t^{1/6}$ = 27·0 μa./millimolar/mg.$^{2/3}$/sec.$^{1/2}$ at 25°) shows that a large number of electrons is involved in the reduction, but the exact number cannot be deduced by application of the Ilkovic equation because the diffusion coefficient of picric acid under these conditions is not known.

When 0·0399 millimole of picric acid in 100 cc. of 0·1 M. HCl was subjected to coulometric reduction, with the potential of the mercury cathode at − 0·65 v., complete reduction to a perfectly colourless solution was obtained after 65 min., and the volume of hydrogen-oxygen evolved in the coulometer was 12·70 cc. (N.T.P.), corresponding to 0·681 m.equ.[13] Hence the number of electrons per mole is 0·681/0·0399 = 17·07, or 17 instead of the 18 electrons expected for complete reduction of the three nitro groups to triaminophenol. Therefore, it appears that reduction

under these conditions yields di-(4-hydroxy-3,5-diaminophenyl)-hydrazine according to the equation



Summary.

A relatively simple potentiostat for automatically maintaining the potential of a working electrode constant during electrolysis is described. Several recent applications of controlled potential electrolysis, particularly with mercury cathodes, are discussed, including separation of metals prior to polarographic analysis, electrolytic preparation of organic compounds, coulometric analysis, and the determination of oxidation states that correspond to polarographic waves observed in complicated reactions at the dropping mercury electrode.

Résumé.

On décrit ici un stabilisateur de potentiel relativement simple, qui maintient constant le potentiel d'une électrode pendant l'électrolyse. On discute plusieurs applications récentes d'électrolyses à potentiel contrôlé, particulièrement avec des cathodes de mercure, comprenant : la séparation préalable de métaux pour une analyse polarographique, la préparation électrolytique de composés organiques, l'analyse coulométrique et la détermination d'états d'oxydation qui correspondent à des ondes polarographiques, observées pour des réactions compliquées à l'électrode à goutte de mercure.

Zusammenfassung.

Ein verhältnismässig einfacher Potentiostat, der automatisch das Potential einer Elektrode während ihrer Benützung in Elektrolyse konstant hält, wird beschrieben. Einige neuere Anwendungen der Elektrolyse mit kontrolliertem Potential—besonders mit Quecksilberkathoden—werden besprochen, darunter die Absonderung von Metallen vor Durchführung einer polarographischen Analyse, die elektrolytische Darstellung organischer Substanzen, coulometrische Analyse und die Identifizierung der Oxydationszustände, die den polarographischen Wellen von komplizierten Reaktionen an der Quecksilbertropfelektrode entsprechen.

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RETARDED ELECTRODEPOSITION OF METALS STUDIED OSCILLOGRAPHICALLY WITH MERCURY CAPILLARY ELECTRODES.

By J. Heyrovský

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The processes which occur in the electrodeposition of metals may be conveniently studied by means of the cathode-ray oscillograph when a mer cury capillary-electrode is polarised with an alternating voltage The potential-time curve ($\pi - t$), or its derivative, the $d\pi/dt - t$ curve,

inform us of the reversibility and rate of the electrode processes involved during very short periods of time of 0·1 to 0·001 sec.

The Experimental Arrangement

The set-up has already been described [1] and is shown in Fig. 1. A is the source of the periodic impulses, R a large variable resistance (up to 1 MΩ.), M is the mercury cell and E, a source of constant voltage. The key K may be connected either to B to obtain the potential-time curves on the

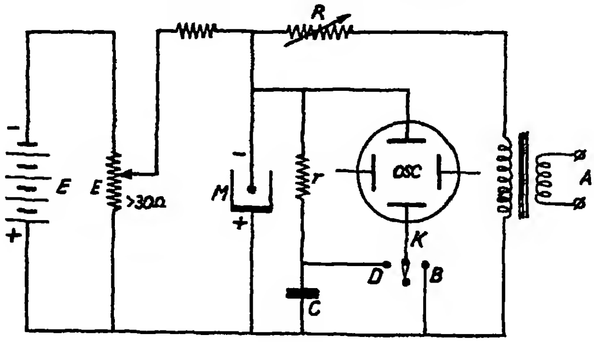

FIG. 1.

oscilloscope, or to D for the derivative curves. A resistance r and condenser C are connected in parallel with the mercury cell. As the source of alternating voltage either the main supply of 50 c.p.s. was used or a rectangular voltage, giving short constant-current impulses periodically changing in direction. The electronic tube generator for the rectangular voltage was constructed by Forejt.

The advantages of using the constant current over the sine-wave current are: (1) the constancy of the impulse allows simple mathematical calculation of the ensuing curves; (2) if dilute electrolytes are used in the

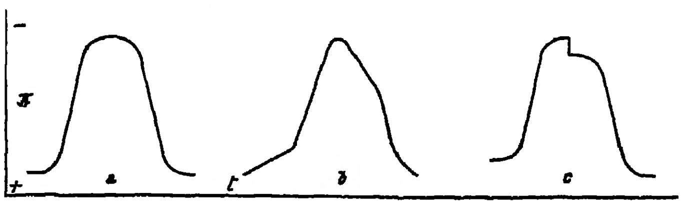

FIG. 2.

cell or large current impulses are necessary, the drop of potential, $i \cdot \rho$, across the cell distorts the potential-time curve *a* (Fig. 2) into *b* (when using the sine-wave current), and only shifts the cathodic branch vertically against the anodic branch by a constant value $2i\rho$ if the constant current, i, is applied (curve *c*).

When concentrated solutions of electrolytes are used, the difference in shape between the potential-time curves obtained with the sine-wave and the rectangular alternating voltage are hardly distinguishable. An oscillograph, Philips type G.M.3156, was used. Oscillograms were taken with exposures of 1/25 sec., when two periods are synchronised on the screen.

[1] Heyrovsky, *Chem. Listy*, 1941, 35, 155; *Polarographie* (Springer, Vienna, 1941), p. 234. Heyrovský and Forejt, *Z. physik. Chem.*, 1943, 193, 77.

The Potential-Time Curves.

If we add to the electrolyte solution a small amount of a depolariser (say a lead salt), which causes electrolysis at a potential lying within those of the chief depolarising processes (i.e., between 0 and $-$ 2 v.), a kink is caused at the potential at which this depolarisation takes place (Fig. 3, where the doted line marks the curve before the admixture). The time-lag at this potential ($-$ 0·5 v.) depends on the concentration of the depolariser, as has been shown previously.[1] Since the cathodic kink is due to the electro-deposition of the depolariser, e.g., to the process

$$Pb^{++} + 2e \rightarrow Pb,$$

and the anodic kink to the reverse process, i.e., $Pb \rightarrow Pb^{++} + 2e$, the

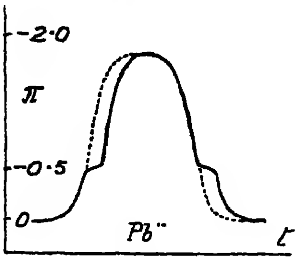

FIG. 3.

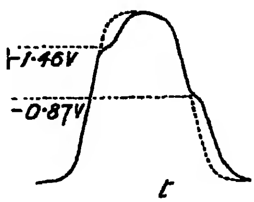

FIG. 4.

two potentials should be identical. This is shown in all solutions of Pb^{II}, and also in those in which Pb^{++} ions form complexes, e.g. in citrates, tartrates, cyanides and alkaline solutions of plumbite, and similarly in all solutions with Tl^{+}, K^{+}, Na^{+}, Cd^{++}, Sn^{++}. We may characterise their depolarising effects as "*oscillographically reversible*".[2] Similar reversibility is encountered in partial reductions and oxidations of cations requiring the transfer of one electron, e.g. $Cu^{++} \rightleftharpoons Cu^{+}$, $Cu^{+} \rightleftharpoons Cu$, $Fe^{+++} \rightleftharpoons Fe^{++}$, $Cr^{+++} \rightleftharpoons Cr^{++}$, $U^{VI} \rightleftharpoons U^{V}$, etc.

However, a strikingly asymmetric potential-time curve is shown in zinc solutions : thus a neutral, acid, ammoniacal or alkaline solution containing

FIG. 5.

Zn^{++} ions gives a curve of the type shown in Fig. 4. The kink due to the cathodic depolarisation is several tenths of a volt more negative than the anodic kink. In a N. $(NH_4)_2SO_4$, N. NH_3 solution with 0·002 N. Zn^{++}, the cathodic potential lies at $-$ 1·46 v. and the anodic at $-$ 0·87 v. When the solutions are warmed up to 90° c., the depolarising potentials come nearer together ; also when the frequency of the alternating current is lowered from 50 to 10 c.p.s., the two potentials approach each other, but in no case are they equal. Mn^{II} and Cr^{II} behave similarly in neutral or ammoniacal solutions. A still larger asymmetry is shown in all solutions of Fe^{II}, Ni and Co ; their curves are shown in Fig. 5. No distinct kink is observable in the anodic branch of these curves.

[2] Heyrovský, *Oesterr. Chem. Ztg.*, 1947, 48, 24; *Chem. Listy*, 1946, 40, 61.

There is, furthermore, a group of ions, including In^{+++}, Bi^{+++}, Sb^{+++}, which show in solutions of the anions SO_4'', NO_3', ClO_4', OH', tartrates, citrates, a marked oscillographic irreversibility, but, in excess of chlorides, a good oscillographic reversibility and an increased rate of electro-deposition. This change is especially marked in the case of indium solutions

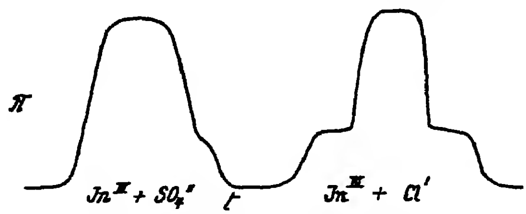

FIG. 6.

(Fig. 6). In this group warming-up makes the cathodic kinks sharper, but does not bring the two depolarisation potentials closer together.

The Derivative Curves.

These are obtained when the key K (Fig. 1) is connected to D. A condenser of the capacity $c' = 0{\cdot}03\ \mu F$ is thus joined in parallel to the electrolytic cell, the capillary electrode of which has a much larger capacity $c(0{\cdot}3\ \mu F)$. The side resistance r is 1000 ohm. Then the potential π of the dropping electrode is practically equal to that of the parallel condenser. Denoting the charges of the condensers by Q and Q' respectively, we have

$$\pi = \frac{Q}{c} = \frac{Q'}{c'} \quad \text{and} \quad d\pi/dt = \frac{1}{c}\frac{dQ}{dt} = \frac{1}{c'}\frac{dQ'}{dt}.$$

Since

$$\frac{dQ}{dt} = i_c \quad \text{and} \quad \frac{dQ'}{dt} = i'_c,$$

we have

$$d\pi/dt = \frac{i_c}{c} = \frac{i'_c}{c'}.$$

Hence the current i'_c, passing through the side condenser and through the resistance r, is shown by the vertical deflexion of the oscilloscope and gives the derivative curve $(d\pi/dt - t)$ as a function of the time.[3] The derivative $d\pi/dt$ thus indicates at any instant the current charging the capillary electrode; it also shows the electrolytic current. This is seen most easily when applying the rectangular voltage, in which case the current, passing the electrolytic cell (if the capacity c' of the side condenser is negligible compared to c) is constant, viz. $i = E/R$. This current, however, is the sum of the capacity (charging) current, i_c, and the electrolytic current, i_E, or $i_c + i_E = i$. Thus any decrease of i_c means an increase of the electrolytic current, i_E. The same is the case when using the sine-wave current, Fig. 7 illustrates this relationship.

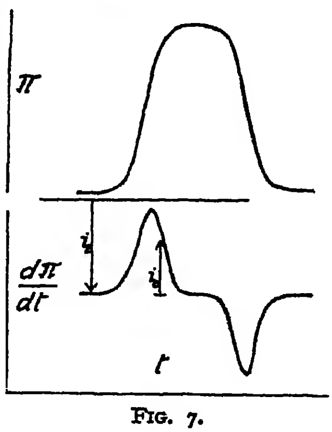

FIG. 7.

The Streaming Electrode.

Since the charging current changes considerably during the growth of the drop, no quantitative measurements are possible from oscillographic

[3] Heyrovský, Šorm and Forejt, *Coll. Czech. Chem. Com.*, 1947, 12, 11.

figures giving derivative curves. To obtain steady oscillograms a streaming electrode had to be introduced. Its latest form is shown in Fig. 8.[4] An A-shaped vessel contains in one arm the capillary (of *ca.* 0·1 mm. inner diam. at the tip), which directs the jet of mercury into the other arm, through which it comes down to the iron crucible; this is filled up to a side hole with mercury. A certain volume, say 18 cc., of the electrolyte solution is poured into the vessel through the lower side tube keeping a constant level, so that the mercury jet has a constant length of some 4 to 6 mm. The side tube allows an inert gas (usually nitrogen) to pass through the solution to free it from atmospheric oxygen. A reservoir with mercury is attached by means of a rubber tube to the capillary and is kept at a height of *ca.* 50 cm. above the tip. Under this pressure the mercury streams out with a velocity of about 100 cm. per sec. If the length of the electrode is 5 mm. and the frequency of the alternating current 50, the mercury jet is renewed four times during one cycle. The amount of mercury flowing out per hour is about 1 kg. The oscillograms obtained with the streaming electrode are perfectly steady and well reproducible, provided the same volume of the solution is used.

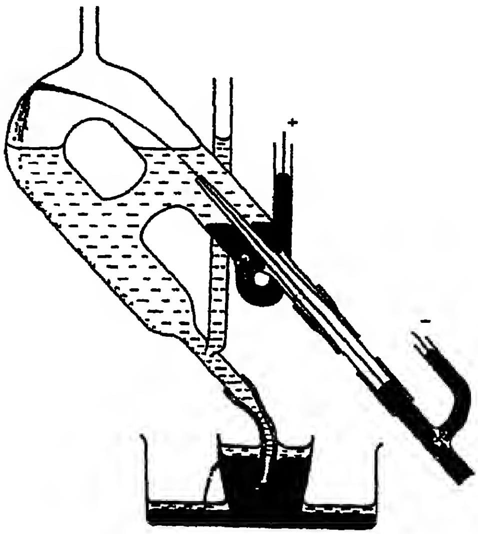

FIG. 8.

For the potential-time curves the slowly-dropping electrode suffices, since its potential is not dependent on the growth of the surface. However, the capacity of the mercury drop changes abruptly as the drop falls off and this causes a sudden change of the oscillographic figure, which, however, does not disturb the observation.

The Use of the Derivative Curve.

Derivative curves are used for quantitative determinations of the rates of electro-deposition. As an example, let us compare the curves due to Cu^{++} ions on one side and Pb^{++} on the other, using N. nitric acid as the indifferent electrolyte (Fig. 9). Curve *a* shows the cathodic branch of the potential-time curve due to 0·001 N. Cu^{++}, *b* that due to 0·001 N. Pb^{++}, at room temperature. We observe that the difference of the (dotted) curve, due to the pure electrolyte, is much more marked in the deposition of lead. Correspondingly the derivative curve also marks a much deeper "cut-in" in the case of lead than when copper is deposited (curves *a'* and *b'*).

Bearing in mind that any decrease of the charging current caused by the addition of the depolariser means the appearance of the electrolytic current due to the electro-deposition of this depolariser, we regard the hatched areas in figures *a'* and *b'* as proportional to the number of coulombs necessary to deposit the Cu^{++} or Pb^{++} ions. Thus the areas limited by the times *t* and *t'* are a measure of the rate of electro-deposition of the metals.[5] This rate is several times greater for the Pb^{++} than for the Cu^{++}

[4] Heyrovský, *Chem. Listy*, 1946, **40**, 222.
[5] Heyrovský, *ibid*, 229.

ions in solutions of nitrates. However, at elevated temperatures the effect of Cu^{++} approaches that of Pb^{++}; the effect of both is equal at ordinary temperature, if excess of Cl′ ions is present. At room temperature, by far the quickest are the depositions of Pb^{++}, Cd^{++} and Tl^{+} ions, both in solutions

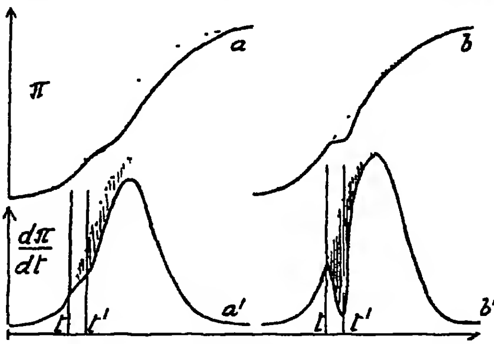

FIG. 9.

of chlorides and nitrates. In ammoniacal solutions the rates of deposition decrease in the series Cd, Co, Ni, Zn.

Hindrance Due to Adsorbed Films.

It has been recently deduced from capacity phenomena displayed in polarography [8] that many molecular species are adsorbed with high velocity as a thin coherent film at the mercury electrode within certain potentials around the "electrocapillary zero" of charge (i.e., − 0·56 v.). Earlier Brdička [9] has produced evidence that numerous organic dyes form adsorbed films, in which the molecules are bound to the surface so that their thermal movement is limited, as in a liquid layer at very low temperatures. Compounds, not reducible at the mercury cathode, e.g. pyridine in alkaline solutions, higher fatty acids in acidic solutions and ether, higher alcohols or phenols in any solution, all form the film suddenly, when the capillary electrode reaches a certain potential more positive than that of the "electrocapillary zero" and this film is at once desorbed, when a more negative

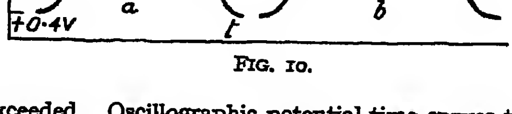

FIG. 10.

potential is exceeded. Oscillographic potential-time curves then have the shape *a* (Fig. 10).

If now small quantities of metallic salts are added, which would cause in the pure indifferent electrolyte depolarisation within the critical potentials of adsorption and desorption of the film, the potential-time curve acquires the form *b* (Fig. 10). We notice that the kink due to the deposition of the metallic ions is shifted to the discontinuity due to the capacity

[9] Brdička, *Z. Elektrochem.*, 1942, 48, 278, 686.

change B, whereas the potential of the anodic kink D remains practically unchanged.

The behaviour represented by Fig. 10b is found in solutions of sulphates, nitrates and hydroxides, when salts of Pb^{II}, Cd, Sn^{II} are present, which otherwise always give symmetrical potential-time curves and the electrodeposition of which is, therefore, regarded as perfectly reversible. If the electrolyte contains Cl′ ions in excess, the influence of the adsorbed film is feeble and the kinks remain symmetrical at the potential of D.

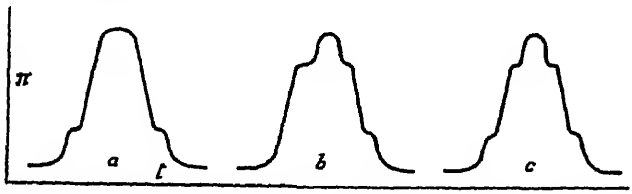

FIG. 11.—Polarographic current-voltage curves with the dropping mercury cathode and saturated KCl-calomel electrode as anode. Curve 3: 0·1 N. K OH in N_2, 0·002 N. $TlNO_3$; curve 4: with 1 % pyridine; curve 5: with 2 % pyridine.

The only metallic ions, whose electrodeposition is not affected by the adsorbed films, are those of Tl^+. The kinks on the potential-time curves due to Tl^+ always remain symmetrical, *no matter which is the indifferent* electrolyte and what sort of adsorbable compounds are added as traces. Fig. 11 characterises the depolarisation effect of Tl^+ ions: a shows the kink due to Tl^+ ions in the pure electrolyte, which may be neutral (chlorides, sulphates, nitrates, etc.), acidic or alkaline. When small quantities of higher alcohols or higher fatty acids are added to the electrolyte (e.g. a small drop to 5 cc.) or larger amounts of ethyl ether, or of a saturated solution of phenol in water, e.g. ½ cc. to 5 cc. of the electrolyte containing Tl^+ ions (*ca.* 0·002 N.), the two thallium kinks remain symmetrical.

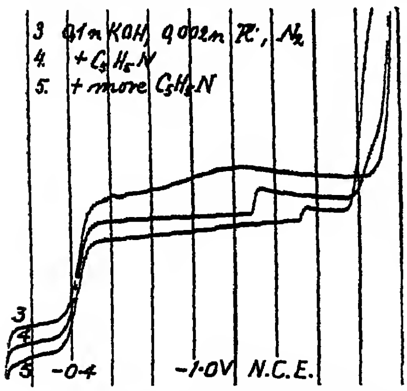

FIG. 12.—Curve 3: 0·1 N. KOH in N_2, 0·002 N. in $Pb(NO_3)_2$; curve 4: with 1 % pyridine.

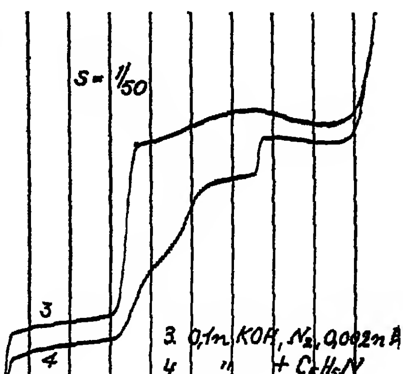

FIG. 13.

Large concentrations of adsorbable matter make the cathodic kink feeble. Similarly when pyridine is added, e.g. 1 or 2 drops, to 5 cc. of N. alkali containing Tl^+ ions, the curve has the shape c, with the Tl^+ kinks unchanged, whereas Pb^{++} ions give curve b (Fig. 11).

This unique behaviour of Tl^+ *ions* manifests itself also on ordinary polarographic current-voltage curves obtained in electrolysis with the dropping mercury electrode. Fig. 12, curve 3, obtained in the pure

electrolyte, shows the regular wave due to the electro-deposition of Tl^+ ions; curves 4 and 5 were obtained after additions of pyridine. The waves at $-0{\cdot}4$ v. are unchanged (the steps around the voltage $1{\cdot}4$ are due to the desorption of the pyridine film). Divalent cations, on the other hand, are greatly hindered in their electro-deposition as shown by the polarogram in Fig. 13. Here a small amount of pyridine produces a profound change of the Pb^{++} wave (curve 4), suppressing the electrolytic current just to the desorption of the film.*

Discussion.

The experiments described above show that the reversibility of the electrode processes, as indicated by the oscillographic potential-time curves, depends on the indifferent electrolyte, on temperature and that it is affected by films of adsorbed molecules. Calling those electrode processes, in which the cathodic and the anodic potential are identical, "reversible", and others, in which the cathodic potential is more negative (and often indistinctly marked) whilst the anodic potential is more positive (and mostly well defined), as "irreversible", we can distinguish four groups of cations.

1. Those having electrode processes which are always reversible, no matter what the electrolyte is, or whether traces of adsorbable compounds are present. The only instances here are the processes, $Tl^+ + e \rightleftharpoons Tl$, and similarly of Li^+, Na^+ and K^+. (The behaviour of Cu^+ ions is near to that of Tl^+.)

2. Ions Pb^{++} and Cd^{++}, which give reversible processes in the presence of any electrolyte (e.g. chlorides, nitrates, perchlorates); these are, however, rendered irreversible by the formation of films of adsorbed molecules. Here excess of chlorides counterbalances the effect of films.

3. Sn^{++}, Bi^{+++}, Sb^{+++}, In^{+++} giving reversible processes when in excess of Cl' (or Br') ions; in the presence of sulphates, nitrates, perchlorates, citrates, tartrates or in alkaline solutions, the processes are irreversible.

4. Divalent ions of the transition elements, i.e., Cr, Mn, Fe, Co, Ni, Cu, Zn, leading to irreversible processes only.

The reduction of Cu^{II}, which proceeds reversibly by the two one-electron transfers, viz. $Cu^{++} + e \rightarrow Cu^+$ and $Cu^+ + e \rightarrow Cu$ is seemingly an exception; however, where the monovalent stage is unstable, e.g. in electro-depositions taking place in excess of NO_3' or SO_4'' ions, the process is irreversible.

Raising the temperature to 70°-90° c. or lowering the frequency of the alternating current impulses diminishes the difference between the cathodic and anodic depolarisation potential.

It may be mentioned that studies of polarisation with an alternating current were carried out by Le Blanc and his co-workers in 1910.[7] Metallic plates, dipping in concentrated solutions of their ions, e.g. Zn in $ZnSO_4$, were made alternatingly cathode and anode and their polarisation was measured. Some metals, such as Pb, Ag, Hg, showed no polarisation. Others, such as Zn, Cu, exhibited a considerable change of potential during the electrolysis which could not be accounted for by concentration polarisation. Le Blanc supposed that such phenomena are due to a delay in the electrolytic processes, caused by a "chemical polarisation", probably caused by the slow rate of dehydration. Our phenomena, showing a difference of the cathodic and anodic depolarisation potential, are, no doubt, of the same nature. In the case of the depolarisation of Zn^{++} ions we must overstep the deposition potential (ordinary half-wave potential being $-1{\cdot}36$ v.) by $-0{\cdot}10$ v. and the potential of anodic dissolution by $+0{\cdot}49$ v. The process of depolarisation exhibits thus a cathodic and anodic "passivity".

* These effects are more fully described in the communication quoted above by Heyrovský, Šorm and Forejt.

[7] Le Blanc, *Abhandl. Bunsenges*, 1910, 3.

Our observations, however, show that the slowness of the process of dehydration cannot play any decisive role in the electro-deposition, since dehydrating agents have but little effect on the potential of the cathodic kink; on the other hand, additions of Cl′ ions render the electrode processes reversible.

Hence the hindrance to the reversibility of the electrode processes has to be sought elsewhere. It is significant that the only permanent reversibility, unhindered by admixtures, is that of the one-electron transfer $Tl^+ + e \rightarrow Tl$. Similarly other processes involving one electron, like $Cu^+ + e \rightarrow Cu$, $Cu^{++} + e \rightarrow Cu^+$, $Fe^{+++} + e \rightarrow Fe^{++}$, etc., have also been found reversible, although not uninfluenced by adsorbable molecules. This suggests that only the acceptance or the surrender of one electron proceeds at the electrode directly and unhindered, whilst the transfer of two or more electrons can never be simultaneous but always successive. Imagine for instance a Zn^{++} ion touching the cathode. During this short impact it may capture only one electron as the probability of two electrons, which strongly repel each other, being transferred simultaneously is very small. The Zn^+ particles recoil at the electrode and have a tendency to diffuse back into the solution, so that the probability of a second contact to accept the second electron is small. Much more probable is the interaction of two freshly formed Zn^+ ions through the dismutation (disproportionation) $2Zn^+ \rightleftharpoons Zn + Zn^{++}$. Consequently instead of a direct capture of two electrons on contact, two Zn^{++} ions must touch the electrode to receive one electron each and then interact to yield the Zn atom, three encounters being thus necessary. This interaction would be hastened by thermal agitation and hindered by adsorbed films in which molecules are anchored to the interface thereby damping the chaotic movement there.

Thus the rate of deposition of Zn^{++} ions has to depend on the rate of dismutation. Although this rate is great, the charging impulse in electrolysis with the alternating voltage proceeds in such a short time (in 0·01 to 0·001 sec.), that dismutation is insufficient to deposit enough atoms to produce a depolarisation kink at the ordinary deposition potential due to the process $Zn^{++} \rightarrow Zn$. Only when the potential of the polarised electrode is nearer to that of the process $Zn^{++} + e \rightarrow Zn^+$, a distinct kink must appear.

The monovalent cations, the formation of which is assumed here to explain the shift of the deposition potential, must be vesy unstable, i.e. the "dismutation constant" K of the equilibrium $2Zn^+ \rightleftharpoons Zn + Zn^{++}$ given as $K = [Zn][Zn^{++}]/[Zn^+]^2$ is very large.

The following relationship gives the value of the potential $\pi_{2,1}$ due to the process $Zn^{++} + e \rightarrow Zn^+$, and $\pi_{1,0}$ due to $Zn^+ + e \rightleftharpoons Zn$ in terms of the potential $\pi_{2,0}$ due to $Zn^{++} + 2e \rightleftharpoons Zn$ and of the dismutation constant K:

$$\pi_{2,1} = \frac{RT}{2F}\ln\left(\frac{[Zn^{++}]}{[Zn^+]}\right)^2 \cdot \frac{k_2}{K}$$

$$\pi_{2,0} = \frac{RT}{2F}\ln\frac{[Zn^{++}]}{[Zn]} \cdot k_2$$

$$\pi_{1,0} = \frac{RT}{2F}\ln\left(\frac{[Zn^+]}{[Zn]}\right)^2 \cdot k_2 \cdot K.$$

The larger the dismutation constant K, the more negative is the potential $\pi_{2,1}$ and the more positive $\pi_{1,0}$. According to this theory the cathodic, more negative kink on the potential-time curve belongs to the process $Zn^{++} + e \rightarrow Zn^+$ and the anodic, considerably more positive kink, is due to $Zn \rightarrow Zn^+ + e$. If $K < 1$, the reduction potential of $Me^{++} + e \rightarrow Me^+$ is more positive than the deposition potential of $Me^{++} + 2e \rightarrow Me$, and the Me^+ ions are stable. No dismutation is involved and hence both reduction steps appear on the polarographic current-voltage curve and two reversible kinks on the oscillographic potential-time curve. This is indeed

found in the case of cupric salts in acidic or ammoniacal solutions containing chlorides.

Note that according to the explanation proposed here, either reaction involved in an "oscillographically irreversible" electrode process may proceed by itself reversibly, yet not as the reversed reaction of the other. Such cases of "irreversibility" arise only when the dismutation velocity is not sufficiently large to bring the ions to equilibrium, otherwise all three potentials $\pi_{2,1}$, $\pi_{2,0}$ and $\pi_{1,0}$ would be equal.

As to the potential $\pi_{1,0}$ of anodic dissolution it might be pointed out that it differs much more from the half-wave potential $\pi_{2,0}$ than $\pi_{2,1}$ does; it is, furthermore, well defined (except for Fe, Ni, Co) and very little affected by various electrolytes or by the formation of adsorbed films. Here the dismutation proceeds probably very close to the electrode surface, between the freshly formed non-hydrated ions unhindered by the aqueous layer.

When considering the readiness with which various cations dismutate to establish the electrode equilibrium, we may deduce that in the electrodeposition of lead and cadmium, the velocity of dismutation is extremely quick, but slower in the deposition of tin, bismuth, antimony and indium, especially in solutions of sulphates and nitrates. It is slowest in the deposition of the transition elements, which are known to fill up the valency electrons into lower electronic levels. This might explain why the dismutation is slower, since the transfer of one electron from one Zn^{+} ion to another has to be carried out from the inner shell of one ion to that in another.

It remains to explain the peculiar action of the Cl′ (or Br′) ions, which change the irreversibility of the trivalent cations of the groups II. and III.

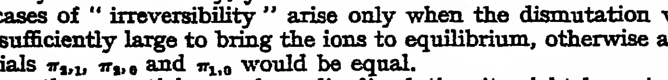

FIG. 14.

(Bi^{+++}, Sb^{+++}, In^{+++}) into oscillographic reversibility. It has to be noted that irreversibility of these cations occurs in solutions containing excess anions SO_4'', NO_3', ClO_4', tartrate, citrate, OH′, all of which are known to be not deformable, i.e. of a rigid electronic structure, unchangeable in an electric field. On the other hand, Cl′ and Br′ ions are deformable, since the centre of their electric charge is shifted in an electric field, so that they become polarised. The fact that the influence of Cl′ ions acts only during the cathodic process, the anodic kink being practically independent of the composition of the solution is also important. The Cl′ ions thus seem to promote the transfer of electrons from the cathode to the cations or between the cations. This facilitation may be imagined as consisting of a convection of the electron through the deformed Cl′ ion, its negative charge gliding on to the cation and at the same time another electron being acquired at the other end of the Cl′ ion from the cathode (Fig. 14) or from another cation.

To act in the above way, the Cl′ ions must have some affinity for the cations to form more or less firmly bound complexes. This is quite acceptable in the case of Bi^{+++}, Sb^{+++}, In^{+++}, Cu^{++}, Cu^{+}.

The great variability of the rates of electrodeposition of metallic cations, as shown by the derivative curves, especially in the case of Cu^{++} or In^{+++} in sulphate solutions on one side and in chlorides on the other must influence the magnitude of the ordinary polarographic diffusion current. Already Fig. 13 shows the large depressive effect due to the adsorbed film, which—according to the theory propounded here—hinders dismutation. Therefore measurements were made of polarographic diffusion currents due to 0·005 N. solutions of Cu^{II}, Tl^{I}, Cd, Zn, Ni, Co, In in N. HCl and in N. KNO_3, K_2SO_4 or H_2SO_4 and, where possible, in N. $NH_3 + NH_4Cl$ and in N. KOH solutions.

These polarographic measurements were carried out by Zajac keeping the same conditions, with 0·05 % gelatine and in an atmosphere of nitrogen. The capillary was 0·07 mm. inner diam., 7·3 cm. length and under 28 cm. of Hg giving an outflow velocity of 0·0027 g./sec. The current-voltage curves were registered keeping the mercury pressure at 57·0, 36·0 and 18·5 cm. in each case. It has been found that in the case of thallous solutions the anions of the excess electrolyte have no influence whatever on the magnitude of the diffusion current. The diffusion currents due to the other cations examined here are 20 to 30 % lower in solutions of sulphates or nitrates than those obtained in chlorides. This accords well with the degree of irreversibility observed oscillographically. In^{+++} ions in solutions of sulphuric or nitric acid, which show no distinct cathodic kink on the potential-time curves, give no polarographic wave.

Where the electro-deposition is retarded, i.e. when the di- or tri-valent ions are not readily discharged, the entire exhaustion of the interphase postulated by Ilkovič for his formula of the diffusion current

$$i_d = 0{\cdot}627\, \nu F D^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}} (c - c_0),$$

viz. that $c_0 = 0$, cannot be reached. Then c_0 has some final value, which depends on the rate of dismutation. The calculations of Ilkovič were based on the assumption that every particle of the depolariser is deposited as soon as it touches the electrode surface. The evidence of this investigation shows, however, that this simple mechanism of electro-deposition only holds for mono-valent cations, but that it involves the above complication for two-electron transfers.

Summary.

An arrangement has been used in which periodic current impulses due to a sine-wave or a rectangular voltage charge a polarisable mercury electrode, of the dropping or streaming type, alternately to negative and positive potentials and the potential-time curves and derivative curves, $d\pi/dt - t$, are observed on the fluorescent screen of a cathode-ray oscilloscope. A frequency of 50 c.p.s. was mostly used. In this way the rates of electrodeposition of metallic cations were studied in different electrolytes.

Electro-depositions involving one-electron transfers, like $Tl^+ \rightleftharpoons Tl$, $Na^+ \rightleftharpoons Na$, $Cu^{++} \rightleftharpoons Cu^+$, $Cu^+ \rightleftharpoons Cu$ and certain two-electron transfers, e.g. $Pb^{++} \rightleftharpoons Pb$, $Cd^{++} \rightleftharpoons Cd$ and $Sn^{++} \rightleftharpoons Sn$ show the cathodic and the anodic depolarisation kink at the same potential; such processes are termed " oscillographically reversible ". The depolarisations due to Bi^{+++}, Sb^{+++} and In^{+++}, shown in solutions of SO_4'', NO_3', ClO_4', OH', tartrates or citrates, produce the anodic kink at a more positive potential than that of the cathodic kink. Such electro-depositions are termed " oscillographically irreversible " and are retarded. Additions of Cl' and Br' ions to these solutions change the irreversible process to a reversible one and increase the rate of deposition. The divalent ions of the transition elements Cr, Mn, Fe, Co, Ni, Cu, Zn are deposited irreversibly in all solutions in which the electrode process involves a two-electron transfer.

From these results it is deduced that the electrolytic acceptance of more than one electron is not simultaneous but consecutive. The second electron is acquired through dismutation, e.g. $2Zn^+ \rightarrow Zn + Zn^{++}$, the velocity of which determines the rate of electro-deposition; this is accelerated by heat and by Cl' ions and is retarded by films of adsorbed molecules.

Résumé.

Des impulsions périodiques de courant, dûes à des voltages de forme sinusoïdale ou rectangulaire, sont employées pour donner des charges alternatives à une électrode de mercure (du type électrode à goutte ou jaillissante) et les courbes, en fonction du temps, du potentiel (π) et de

($d\pi/dt - t$) sont observées sur un oscillographe à rayon cathodique. Les vitesses de dépôt électrolytique sont étudiées de cette façon pour divers métaux dans différents électrolytes. On trouve que les dépôts, qui comportent le transport d'un électron (ou de deux dans certains cas) sont " réversibles à l'oscillographe " (c'est à dire que les dépolarisations anodique et cathodique se manifestent au *même* potentiel) ; d'autres dépôts, de quelques métaux dit et trivallents, sont " irréversibles à l'oscillographe," mais sont rendus " réversibles " par addition d'ions Cl à l'électrolyte. On conclut que deux électrons sont toujours tranférés consécutivement à cause de la dismutation (par exemple $2Zn^{+} \rightarrow Zn + Zn^{++}$), dont la vitesse détermine celle du dépôt ; cette dernière est accélérée par la chaleur ou par des ions Cl, mais est retardée par des films de molécules adsorbées.

Zusammenfassung.

Periodische, durch sinuswellenförmige oder rechteckige Wechselspannungen hervorgerufene Stromimpulse werden benützt, um einer (tropfenden oder strömenden) Quecksilberelektrode wechselnde Ladungen zu geben ; die Potential (π) — Zeit (t) und $d\pi/dt - t$ Kurven werden mit Hilfe eines Kathodenstrahloszillographen bestimmt. Auf diese Weise wird die Geschwindigkeit der elektrolytischen Abscheidung verschiedener Metalle untersucht. Es wird gefunden, dass Abscheidungen, in denen nur ein Elektron transferiert wird (und bestimmte Zweielektronenreaktionen) „ oszillographisch reversibel " sind (d.h. sie zeigen anodische und kathodische Knicke am selben Potential, während andere Abscheidungen (z.B. von zwei- und drei-wertigen Metallen) „ oszillographisch irreversibel " sind, aber durch die Hinzufügung von überschüssigen Chloridionen zur Elektrolytlösung reversibel gemacht werden können. Hieraus wird gefolgert, dass zwei Elektronen immer nacheinander durch Dismutation transferiert werden (z.B. $2Zn^{+} \rightarrow Zn + Zn^{++}$) und dass die Geschwindigkeit dieser Reaktion, die von Chloridionen und Wärme beschleunigt, aber von adsorbierten Molekülfilmen verzögert wird, für die Abscheidungsgeschwindigkeit bestimmend ist.

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(*b*) *GENERAL DISCUSSION* *

Dr. J. N. Agar (*Cambridge*) said : The formation of cavities within the steel of the " decomposer," described by Hoogland, is a clear indication of the presence of considerable quantities of atomic hydrogen. This is a very important observation, but in order to see its true significance it is essential to know whether the hydrogen enters the steel by diffusion through the mercury or directly, at points where the steel is in contact with the electrolyte. At such points the steel forms the cathode of a short-circuited cell,

Na(Hg)	NaOH		Fe
—	$\rightarrow Na^{+}$	H^{+}—	$\rightarrow$

and the passage of hydrogen into and through steel cathodes is a well-known phenomenon, although it is usually considered to be more marked in acid than in alkaline solutions.

* On three preceding papers.

It appears that hydrogen entering the steel above the level of the mercury would have to diffuse rather a long way in order to reach the locality where cavities are formed, and one would expect to find at least some cavities nearer to the point of entry. Is it possible that a thin film of solution creeps round between the mercury and the steel, so that a cell of the above type is set up close to the observed cavities?

It is not necessary to assume that hydrogen atoms play any part in the cathodic reduction of oxygen to hydrogen peroxide. The reaction can be formulated in terms of transfer of electrons from the cathode to oxygen molecules, followed by reaction with hydrogen ions, e.g.,

$$O_2 + 2e \rightarrow O_2^{--}$$
$$O_2^{--} + 2H^+ \rightarrow H_2O_2$$
$$(\text{or } O_2^{--} + H^+ \rightarrow HO_2^-$$

in strongly alkaline solution).

In reality, these reactions may well take place by one-electron steps, e.g.,

$$O_2 + e \rightarrow O_2^-$$
$$O_2^- + H^+ \rightarrow HO_2$$
$$HO_2 + e \rightarrow HO_2^-, \text{ etc.}$$

The polarographic wave for reduction of O_2 to H_2O_2 in acid solutions occurs at about + 0·2 v. on the hydrogen scale, and I have recently found that the rate of reduction at a stationary Hg cathode becomes appreciable at about the same potential. It is unlikely that the concentration of hydrogen atoms on a mercury surface is significant at such positive potentials and it is therefore probable that reduction proceeds in the manner indicated above. This does not, of course, exclude the possibility that hydrogen atoms play a part at more negative potentials.

Finally, I would suggest that the decrease in yield of H_2O_2 after contaminating the mercury by contact with V2A steel might be due to catalytic decomposition of the H_2O_2, rather than to inhibition of its formation.

Dr. J. Weiss (*Newcastle*) (*communicated*): With reference to Hoogland's paper, it is known [1] that the formation of hydrogen peroxide from H atoms and molecular oxygen takes place according to the reactions:

$$H + O_2(+ M) = HO_2(+ M)$$
$$2HO_2 = H_2O_2 + O_2$$

accompanied by a small formation of ozone according to:

$$2HO_2 = O_3 + H_2O.$$

Prof. A. Frumkin (*Moscow*) (*communicated*): In connection with the interesting results communicated in the paper of Prof. Heyrovsky, I should like to draw attention to a paper by Loshkarev, Sotnikova and Krjukova.[2] These authors found that the value of the current during the electro-deposition of Sn from an acid $-SnSO_4$ bath is greatly reduced in the presence of certain organic compounds, like diphenylamine, thymol, α- and β-naphthol and others. The effect disappears at a certain cathodic polarisation which is closely related to the potential which causes a desorption of these compounds from a mercury-solution interface and which can be determined by electrocapillary measurements. It is probably closely related to the effect described by Heyrovsky, as well as to the suppression of the cystine wave by camphor and thymol.[3] In the experiments of Loshkarev *et al.* so long as the desorption potential was not attained the current remained in a certain polarisation range independent of the potential although much smaller than the normal diffusion current. In my opinion the rate-determining step in this case is the penetration of the Sn ions through the adsorbed layer of organic molecules to the metal-solution interface.

[1] Weiss, *Trans. Faraday Soc.*, 1935, **31**, 668.
[2] *J. Physic. Chem.* (*Russ.*), 1947, **2**, 219.
[3] Kolthoff and Barnum, *J. Amer. Chem. Soc.*, 1941, **63**, 520.

The accelerating influence of the Cl′ and Br′ ions on the discharge of trivalent cations observed by Heyrovsky can be accounted for by the change in the structure of the double layer caused by anion adsorption. The effect is similar to the lowering of hydrogen overvoltage observed when adsorption of anions sets in.

Mr. A. W. Hothersall (*Woolwich*) said, in concluding the Discussion: Two chief topics have been raised in this Discussion. The first was the current distribution in an electroplating bath and how it was affected by conductivity and polarisation. There were two different schools of thought—one approaching the problem from a theoretical angle and reaching a different conclusion from the other which was approaching it more from practical experience. He would leave the individual authors to deal with the points raised with the reminder that such differences of opinion originated frequently from differences in definitions of terms used.

The second main point raised was the structure of the metallic deposit, especially near the interface with the underlying metal. Prof. Ubbelohde had raised the important question of stress in the first layers of metal deposited. One would expect that there must be a transition stage during which the atomic spacing of the deposited metal adjusted itself to that of the basis metal; some years ago Cochrane had shown that, when nickel was deposited upon copper, the atomic spacing of the nickel, which was initially similar to that of copper, gradually shrank to that of nickel. Further information and confirmation was needed especially for combinations of deposit and basis metal where the difference in atomic spacing was greater than the 15 % referred to as a limiting factor by Finch, Wilman and Yang. It was also important to note that, as pointed out by Ollard, the microscope could be a valuable tool for studying what happened in the early stages of deposition but here, as in the use of electron diffraction, it was most important that detailed attention should be given to the technique of preparation of the metal for deposition as well as to meticulous control of the conditions of deposition. It should also be remembered that polished sections seen under the microscope gave a two-dimensional picture only and that there was some temptation to extend their interpretation to three dimensions (as Ollard appeared to have done in speaking of filling up crevices).

These general considerations and the remarks of Prof. Allmand and others, suggesting a possible relationship between the abnormal structure of metallic deposits and metal overpotential, emphasised the necessity for periodical discussions between electrochemists studying the events in the electrolyte and physicists and metallurgists investigating the structure of the resultant product.

IV. OXYGEN OVERVOLTAGE

Introductory paper.

By A. Hickling.

In considering anodic processes we are confronted with a mass of experimental data which so far lacks, to a great extent, any satisfactory unifying theory. Of the many problems which confront us, I would select three as being of outstanding importance. They are:

(*a*) the mechanism of the discharge of the hydroxyl ion at an anode and of oxygen evolution;

(*b*) the part played by the electrode material in anodic processes and the mechanism of anodic passivity; and

(*c*) the mechanism of electrolytic oxidation reactions at an anode.

Let me say a few words about each of these problems, which are of course intimately related, in turn.

The mechanism of hydroxyl ion discharge and oxygen evolution must be directly involved in the occurrence of oxygen overvoltage or overpotential, and studies of this phenomenon should therefore throw light

upon the problem. The fact that the potential of an anode must be raised to a value appreciably more positive than the theoretical reversible oxygen potential to secure oxygen evolution has been known for well over 40 years, and fairly extensive measurements of the so-called "minimum" oxygen overvoltages, i.e. the excess potentials at the commencement of oxygen evolution, were made quite early in the history of the subject. Attempts to measure oxygen overvoltages at definite c.d.'s, however, met with considerable experimental difficulties, in particular that of obtaining reasonable reproducibility in the results, and it is only within the last 20 years that measurements with any claim to precision have been made. Even so there has been a tendency, which I personally think is unfortunate, to study platinum exclusively as anode material. While platinum has obvious experimental advantages, conclusions drawn from the study of this one anode material may not be universally valid, and there is still considerable obscurity about the dependence of oxygen overvoltage upon such variables as electrode material, c.d., time, temperature, environment of the OH′ ion, etc. In these circumstances speculation seems somewhat premature and the theories which have been put forward seem to have been formulated largely by analogy with the more thoroughly investigated phenomenon of hydrogen overvoltage.

The ideas of the part played by the electrode material in anodic processes were formerly largely speculative, but in recent years considerable direct evidence has been accumulated by the experimental method pioneered by Bowden and Rideal, and by Butler, of studying oscillographically the rapid changes of potential during the initial build-up of polarisation at an anode. By working at constant c.d., and recording the variation of potential with quantity of electricity passed prior to oxygen evolution, it is possible to detect and identify with certainty the various processes occurring, such as the charging of double layers and the formation of oxide films. Now that the experimental difficulties of the method have been largely overcome, and the cathode ray oscillograph has been adapted as an indicating instrument, data for different materials are rapidly accumulating and should prove of great value in elucidating the part played by the anode material in oxygen evolution and the way in which anodic passivity is brought about.

Electrolytic oxidation reactions are remarkable for the varied nature of the products formed, the very complex dependence of the results on such variables as nature of anode material, c.d., temperature, *p*H, presence of foreign substances, etc., and the peculiar way in which, in many cases, the anode potential is connected with the reaction occurring. In a very few cases, such as the oxidation of ferrous and ferrocyanide ions, the process satisfies all the criteria of a thermodynamically reversible oxidation-reduction reaction and the anodic process may be regarded simply as the removal of electrons from the depolariser. In the great majority of cases, however, this simple view is quite inadequate to explain the very complex experimental phenomena and one is driven to postulate the existence of some chemical oxidising agent at the anode. Gaseous molecular oxygen is unable to bring about many of the electrolytic oxidations which are observed, and it would therefore appear that some intermediate product which is transiently produced between the discharge of the OH′ ion and the evolution of gaseous oxygen must be the active oxidising agent. Various suggestions have been made as to the nature of the active substance or substances, and the OH radical, hydrogen peroxide, atomic oxygen, and oxides formed with the anode material have been postulated by various workers. The position at present is one of considerable controversy.

These, which I have very briefly summarised, are some of the main lines upon which the study of anodic processes is proceeding, and we have a number of papers on each of these branches before us for discussion to-day.

SOME ANOMALIES IN THE CONCEPT OF ELECTRODE POTENTIAL AS THE DETERMINING FACTOR IN THE OCCURRENCE OF ANODIC REACTIONS.

By A. Hickling.

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I.

According to current electrochemical concepts the factor that determines which of a number of possible electrode reactions will occur on passage of current is the potential at which each process can take place, it being generally taken as axiomatic that at a cathode the process requiring the least displacement of the potential of the electrode in a negative direction, and at an anode that requiring the least displacement in a positive direction, will necessarily occur in preference to any others. This view, which seems entirely reasonable, accounts very satisfactorily for the order in which all cathodic processes occur, but with anodic processes there are numerous apparent exceptions to it, and it is the purpose of the present paper to draw attention to these anomalies which do not seem hitherto to have been sufficiently realised and which constitute a formidable problem for any general theory of anodic reactions.

II.

Many examples of these anomalies could be cited, but it is desired here merely to quote two cases in which the paradox is very clearly displayed.

A particularly good example is shown in the occurrence of the Kolbe reaction in aqueous solution. In the electrolysis of a mixture of M. potassium acetate + M. acetic acid with a smooth platinum anode at 20° C. with a current density (c.d.) of 0·1 to 1 amp./sq. cm., ethane and carbon dioxide are the main anodic products (Kolbe reaction) and are formed with a current efficiency of *ca.* 90 %, the net reaction being formally represented as $2CH_3COO' + 2F = C_2H_6 + 2CO_2$, and the anode potential observed is about 2·4 v. on the hydrogen scale.[1] The potential at which oxygen can be evolved at the same anode and under identical conditions from a buffer solution of equal hydrogen ion concentration not containing acetate ions is approximately 2·0 v. Furthermore, if the Kolbe reaction occurring at 2·4 v. is inhibited, which can be achieved in a variety of ways, e.g., by the addition of a little manganous sulphate to the acetate mixture, the potential promptly falls to about 2·0 v., the anodic process then being oxygen evolution + oxidation of the acetate to methyl alcohol. Here then the experimental results indicate that the Kolbe reaction requires a potential some 0·4 v. higher than that of alternative anodic reactions, ***and yet it is the Kolbe reaction which normally occurs.***

The discrepancy is even greater in the occurrence of the Crum Brown-Walker synthesis in aqueous solution, i.e., in the anodic formation of the ester of a dibasic acid by electrolysis of a solution of an ester-acid salt containing half the number of CH_2-groups of the final product. Thus if a mixture of M. potassium ethyl malonate + M. hydrogen ethyl malonate is electrolysed with a smooth platinum anode at 10° C. with a c.d. of 0·1 to

[1] Hickling and Westwood (unpublished observations); see also Glasstone and Hickling, *J. Chem. Soc.*, 1934, 1878; *Chem. Rev.*, 1939, **25**, 407. The potentials quoted in this and the subsequent example were measured by the interrupter method (Hickling, *Trans. Faraday Soc.*, 1937, 33, 1540) and are thus free from any resistance errors; if there is any error in the quoted values it would be in the direction of making them *lower* than the true values.

1 amp./sq. cm., diethyl succinate and carbon dioxide are the main anodic products and are formed with a current efficiency of *ca.* 70 %, the net reaction being formally represented as $2CO_2Et \cdot CH_2 \cdot COO' + 2F = CO_2Et \cdot CH_2 \cdot CH_2 \cdot COOEt + 2CO_2$, and the anode potential observed while this process is occurring is about 2·8 v. on the hydrogen scale.[2] The potential at which oxygen can be evolved under the same conditions, as shown either by working with a solution of the same hydrogen ion concentration not containing ethyl malonate ions or by inhibiting the synthesis in the ethyl malonate electrolyte, is only about 2·0 v. Here then the potential measurements would suggest that the Crum Brown-Walker synthesis requiring the very high potential of 2·8 v. should never occur in aqueous solution, but that the alternative process of oxygen evolution requiring a potential some 0·8 v. less positive should have precedence, *and yet it is the Crum Brown-Walker synthesis in practice which mainly occurs under ordinary conditions.*

III.

It might be suggested to explain these anomalies that in the presence of acetate and ethyl malonate ions the process of oxygen evolution is retarded in some way and the oxygen overvoltage is thereby raised considerably. Such an explanation is not only unsatisfactory in that it is of a purely *ad hoc* nature but would seem to break down on the following grounds.

(*a*) At anodes other than smooth platinum, e.g., platinised platinum, gold, lead dioxide, etc., the Kolbe and Crum Brown-Walker reactions do not take place with substantial current efficiencies and the anode potentials observed are quite normal and closely similar to those of oxygen evolution observed in other electrolytes of the same pH values.

(*b*) The current efficiencies of the Kolbe and Crum Brown-Walker reactions occurring at a smooth platinum anode can be greatly diminished in a variety of different ways, e.g., by lowering of c.d. or concentration, by rise of temperature, by addition of catalysts for hydrogen peroxide decomposition, by addition of large quantities of foreign anions, etc., and in all these cases the anode potential falls and approaches a normal oxygen evolution value.

IV.

It thus appears difficult in the examples quoted to avoid the conclusion that the anode potential is the *result* of the reaction taking place rather than the factor which determines which reaction shall occur, and evidence from other studies of electrolytic oxidation strongly suggests that this may generally be the case.[3] Electrochemical theory is, however, still confronted with the problem as to why a process giving rise to a high potential should take place in preference to one which leads to a lower potential. A conceivable mechanism has been advanced previously by the present author [3] which assumes that the initial anodic process involves an irreversible stage and that the potentials observed are set up indirectly by subsequent reactions, but this view involves some difficulties, and it is in the hope that some simpler explanation may be advanced that the problem is raised here.

Summary.

Some anodic reactions are described in which processes occur at a high positive potential in preference to other possible reactions requiring or leading to much lower potentials. The problem that these anomalies provide in the light of current electrochemical theory is emphasised.

[2] Hickling and Westwood, *J. Chem. Soc.*, 1938, 1039; Glasstone and Hickling, *Chem. Rev.*, 1939, 25, 407.

[3] Glasstone and Hickling, *loc. cit.*[1]

Résumé.

On décrit quelques réactions anodiques, qui se produisent à un haut potentiel positif, de préférence à toute autre réaction possible, qui exigerait des potentiels beaucoup plus bas ou conduirait à de tels potentiels. On souligne les problèmes que constituent ces réactions, regardées comme des anomalies selon la théorie électrochimique courante.

Zusammenfassung.

Einige anodische Reaktionen werden beschrieben, bei denen Prozesse, die ein höheres positives Potential erfordern, anstelle von anderen möglichen Reaktionen, die ein niedrigeres Potential erfordern oder zu einem solchem führen würden, stattfinden. Die Probleme, die von diesen Widersprüchen zur gegenwärtigen elektrochemischen Theorie aufgeworfen werden, werden hervorgehoben.

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ELECTROLYTIC POLARISATION: III. THE EFFECT OF THE SOLVENT ON THE OXYGEN OVERPOTENTIAL.

BY J. O'M. BOCKRIS.

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As is well known, electrolytic evolution of oxygen at an anode in acid or alkaline solution is generally associated with an overpotential of the same order as that occurring during hydrogen evolution.[1] The theories advanced to explain the phenomena associated with the overpotential of oxygen can be divided into three groups, depending upon which of the following reactions is considered to limit the velocity of evolution of oxygen from the anode surface: (i) the heterogeneous combination of oxygen atoms to molecules (Foerster *et al.* [2]), (ii) the discharge of OH^- to the hydroxyl radicle (Gurney [3]), (iii) the transfer of a proton from the anode to a water molecule in the vicinity of the anode (Eyring, Glasstone and Laidler [4]). It would be premature to discuss in detail the relative likelihood of any of these groups from the published experimental evidence on oxygen overpotential [5] which is meagre and often described too briefly to make easy assessment of its reliability.

[1] For review, see Klemenc, *Z. physik. Chem.*, 1939, **185**, 1.

[2] *Z. Elektrochem.*, 1910, **16**, 353; *Electrochemie wässeriger Lösungen*, 1922, 335.

[3] *Proc. Roy. Soc. A*, 1931, **134**, 137; 1932, **136**, 378; see also Wolfenden, *Ann. Reports*, 1932, 34.

[4] *J. Chem. Physics*, 1939, **7**, 1053; *Trans. Amer. Electrochem. Soc.*, 1939, **76**, 331; Kimball, Glasstone and Glassner, *J. Chem. Physics*, 1941, **9**, 91; but see Frumkin, *Acta Physicochim.*, 1940, **12**, 481.

[5] Foerster, *Z. physik. Chem.*, 1909, **69**, 236; Glasstone, *Trans. Chem. Soc.*, 1923, **123**, 1745; Knobel, Caplan and Eisemann, *Trans. Amer. Electrochem. Soc.*, 1923, **123**, 55; Mazuschelli and Romani, *Gazetta*, 1927, **52**, 524; Bowden, *Proc. Roy. Soc. A*, 1929, **126**, 107; Butler and Armstrong, *ibid.*, 1932, **137**, 604; Hoar, *ibid.*, 1933, **142**, 628; Butler and Drever, *Trans. Faraday Soc.*, 1936, **32**, 427; Roiter and Jampolskaya, *Acta Physicochim.*, 1937, **7**, 247; Pearson and Butler, *Trans. Faraday Soc.*, 1938, **34**, 1163; Hickling, *ibid.*, 1945, **41**, 333; 1946, **42**, 518.

It does seem possible, however, to extend to oxygen overpotential investigations an examination which appears to have been of some use in giving definite and unambiguous evidence against certain theories of hydrogen overpotential.[6] Thus it appears that an examination of the solvent effect on oxygen overpotential would give cogent evidence concerning the importance of the environment of the OH^- ion to the potential of the working anode and the validity of the postulate of prototropic transfer as the slow stage. Additional interest attaches to the results of oxygen overpotential measurements in aqueous solution also recorded, as these have been made using a new procedure for the method of measurement (see below). No previous work on the effect of the solvent on the oxygen overpotential appears to have been reported in the literature.

Experimental.

Choice of System.—The principal requirements of an ideal solvent for the present work are as follows.

(i) It must have good ionising properties so that appreciable currents can easily be passed through its solutions and so that ohmic overpotential is reduced to a minimum.

(ii) It must have a good solvent power for, and stability to, a suitable electrolyte, e.g. sulphuric acid.

(iii) It must be easily purified, preferably without the aid of metal ions.

(iv) It must be stable to nascent oxygen.

This last point severely limits the number of possible solvents. Thus, the primary alcohols, glycol, acetone, formic acid, etc., are rapidly oxidised at a platinum anode,[7] in most cases easily. The aliphatic ethers and similar solvents are unsuitable because of the lack of ionising power and miscibility with water. A detailed examination of the properties of a considerable number of solvents shows that it is not possible to obtain a solvent which obeys all the above criteria: acetic acid * and 1 : 4 dioxan represent, however, substances which do not seem to be oxidised at a platinum anode at high current densities in acid solution. It is not practical to use an anhydrous solution of these substances with sulphuric acid owing to the very high resistance of the solution, but a full range of mixed solvents may be used and the results extrapolated to the value for the anhydrous solvents.

Smooth platinum was used as the electrode material because relatively reproducible results have been reported by other workers for measurements with this substance in aqueous solutions.[9] It does not appear of value to extend the work to other types of systems at present owing to the complicating effects of oxidation both of electrodes and solvents, which are known to occur.

Apparatus.—The experimental cell has been previously described.[10] Modifications made for the present experiments consisted in the replacement of the hydrogen stream to the cathode compartment by one of oxygen to the anode compartment. This stream was directed on to the platinum anode, which consisted of a platinum wire of total area 0·1 sq. cm., rolled into a spiral form and supported vertically by means of a

* The Kolbe reaction is inhibited by sulphuric acid (see [8]).

[6] Bockris (in course of publication); *Nature*, 1946, **158**, 584.

[7] Primary alcohols: Elbs and Brunner, *Z. Elektrochem.*, 1900, **6**, 604; Koidzumi, *Mem. Coll. Sci. Kyoto*, 1928, **11A**, 391. Glycol: Löb., *Z. Elektrochem.*, 1910, **16**, 1. Formic acid: E. Muller, *ibid.*, 1923, **29**, 264; Herasymenko, *Ukraine Chem. J.*, 1929, **4**, 439. Acetone: Bradt and Opp, *Trans. Amer. Electrochem. Soc.*, 1931, **59**, 81.

[8] Glasstone and Hickling, *J. Chem. Soc.*, 1934, 1878.

[9] Foerster and Pigwet, *Z. Elektrochem.*, 1904, **10**, 714; Knobel, Caplan and Eisemann, *loc. cit.*, ref.[5]. Glasstone, *Trans. Chem. Soc.*, 1923, **123**, 1745.

[10] Bockris, *Trans. Faraday Soc.* (in press).

glass tube inserted into the rubber bung of the anode compartment. Pretreatment of the anode consisted in washing in hot conc. HCl, hot conc. HNO_3, and water and then heating to redness. The cathode consisted of a sheet of platinum foil, 1 sq. cm. in area. The experiments were carried out at room temperature without special attention to temperature control, which, having regard to the temperature coefficient of oxygen overpotential, introduced negligible changes in condition.[11]

Purification of Solvents.—Acetic acid was purified according to the method of Orton, Edwards and King,[12] namely, addition of sufficient P_2O_5 to convert all the water to phosphoric acid, and then distillation; m.p. fd. 16·5°.

Technical dioxan was dried with KOH and BaO, distilled from the latter, and then from Na, the portion boiling at 101-102° being collected. It was redistilled from sodium as required (m.p. fd. 11·75).

The water used was ordinary distilled water redistilled in a Pyrex all-glass apparatus in the presence of acid $KMnO_4$.

General Procedure.—The appropriate quantity of acetic acid or dioxan was introduced in air into a solution of aqueous H_2SO_4 of strength such that the whole solution was molar with respect to H_2SO_4. Oxygen from a cylinder was passed through acid $KMnO_4$, conc. H_2SO_4, water and a bubbler containing the solution to reduce the tendency of the gas to alter the composition of the electrolyte. Oxygen was passed for about $\frac{1}{2}$ hr. through the solution before the latter was introduced into the Pyrex electrolytic cell. The potential of the platinum anode was observed against a hydrogen electrode until it had attained a state of approximate constancy.* Polarisation was then commenced at a c.d. of 10^{-3} amp. per sq. cm. The build-up of potential with time was followed until approximate constancy had been attained, the current switched off and the electrode allowed to rest until its potential had again attained an approximately constant value. The same procedure † was then repeated for c.d. of 10^{-2}, 5×10^{-2} and 10^{-1} amp./sq. cm. Each set of polarisations in a given system, which lasted generally 10-12 hr., was carried out at least 3 times. The cell was cleaned with chromic-sulphuric acid between each experiment, for which a fresh platinum anode was always used. The reproducibility varied between $\pm$ 0·01 and $\pm$ 0·03 v. It was better in aqueous than in mixed solvents.

Results.

Results for the effect of solvent composition and c.d. are shown respectively in Figs. 1, 2, 3 and 4, and are summarised in Table I where the experimental values of b, the value of the coefficient in Tafel's equation $\eta = a + b \log I$ (η = overpotential, I = current density, a and b are constants), obtained from the initial slopes of the η-log I lines, are also included.

The variation of overpotential with time did not seem to be essentially affected by the solvent. The potential of the hydrogen-oxygen cell before polarisation attained approximate constancy at about 0·9 v. in all systems. Anodic polarisation caused a slow increase with time, generally having a magnitude of less than 2 centivolt/hr. after 2-3 hr. polarisation. After cessation of the polarising current the potential of the smooth platinum electrode decayed to 1·4-1·2 v. in some 2-3 min. and thereafter slowly to about 0·9 v. in the succeeding 1-2 hr.

[11] Foerster, *loc. cit.*, ref.[8].

[12] *J. Chem. Soc.*, 1911, 99, 1178.

* Approximate constancy was taken to mean a change of less than 1 centivolt in $\frac{1}{4}$ hr. (cf. [14]).

† Cf. use of a similar technique of resting between each polarisation at different c.d. used in hydrogen overpotential measurements.[13]

TABLE I.

Non-aqueous Component.	% Water.	Overpotential. c.d. amp./sq. cm. 10^{-3}.	10^{-2}.	5×10^{-2}	10^{-1}.	b.
Acetic acid . .	100	0·62	0·79	0·89	0·92 [1]	0·16 [2]
	75	0·87	1·23	1·47	1·57	0·35
	50	0·92	1·31	1·53	1·64	0·34
	25	0·98	1·38	1·59	1·71	0·35
	0 [3]	0·99	1·38	1·59	1·70	0·35
Dioxan . .	90	0·68	0·93	1·08	1·09	0·25
	75	0·72	1·01	1·10	1·15	0·24
	50	0·79	1·16	1·28	1·33	0·30
	35	0·90	1·18	1·31	1·38	0·27
	22	0·87	1·15	1·34	1·39	0·27
	0 [3]	0·82	1·09	1·35	1·40	0·27

[1] Pretreating the platinum anode by washing with water and wiping with filter paper just before introduction into the solution the corresponding results for aqueous solutions at these four c.d.'s were: 0·78, 0·90, 1·01, 1·05.

[2] Values for b in Tafel's equation for aqueous solutions obtained by other workers are:

Glasstone [17] (c.d. range 10^{-2}-10^{-1} amp./sq. cm.), 0·06;

Knobel, Caplan and Eisemann [18] (c.d. range 10^{-3}-10^{-2} amp./sq. cm.), 0·13-0·33;

Bowden [15] (c.d. range 10^{-4}-10^{-3} amp./sq. cm.), 0·11;

Roiter and Jampolskaya [19] (c.d. range 10^{-4}-10^{-3} amp./sq. cm.), 0·14.

The values of these workers are not strictly intercomparable owing to the different c.d. ranges examined and techniques employed in measurement.

[3] Extrapolated—it must be stressed that the linear extrapolation used is quite arbitrary. Measurements at higher non-aqueous contents are not practical by the direct method. All potentials recorded are on the hydrogen scale.

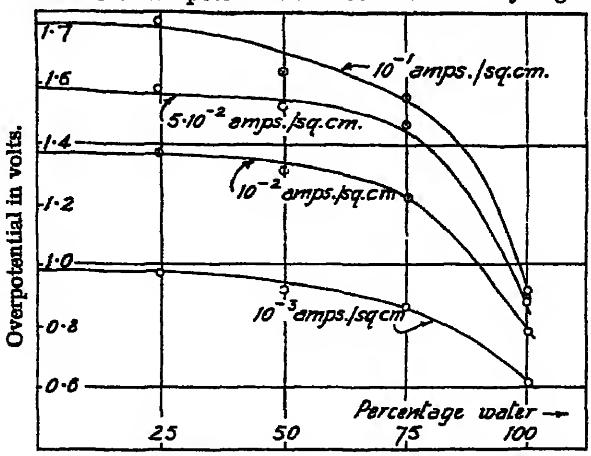

FIG. 1.—Oxygen overpotential on platinum in acetic acid-water mixtures (N . H_2SO_4).

[13] Hickling and Salt, *Trans. Faraday Soc.*, 1940, 36, 1226.
[14] See ref.[13].
[15] Bowden, *loc. cit.*, ref.[5].
[16] Butler and Thompson, *Proc. Roy. Soc., A*, 1933, 141, 86.
[17] Glasstone, *loc. cit.*, ref.[3].
[18] Knobel, Kaplan and Eisemann, *loc. cit.* ref.[5].
[19] Roiter and Jampolskaya, *loc. cit.*, ref.[8].

Discussion.

Conclusions from the results of Table I and Fig. 1-4 may be briefly summarised.

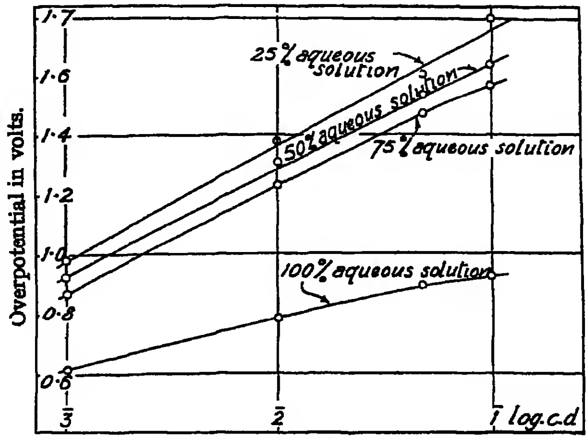

FIG. 2.—Oxygen overpotential on platinum in acetic acid-water mixtures (N. H_2SO_4).

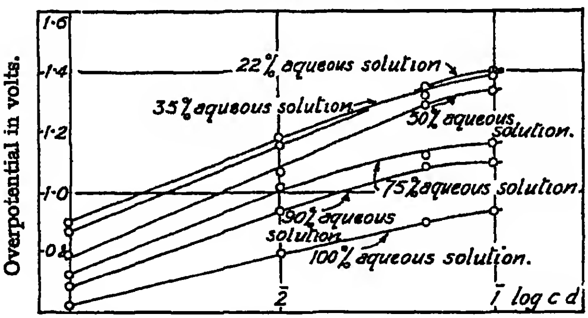

FIG. 3.—Oxygen overpotential on platinum in dioxan-water mixtures (N. H_2SO_4).

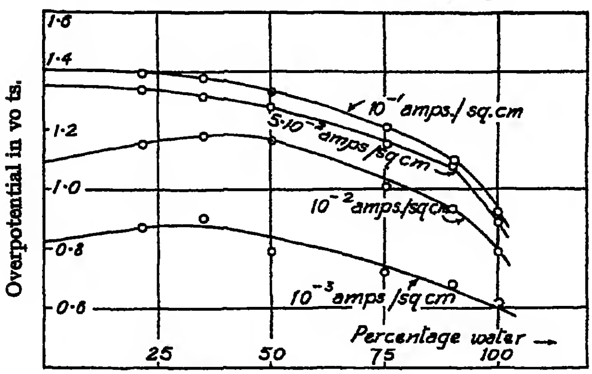

FIG. 4.—Oxygen overpotential on platinum in dioxan-water mixtures (N. H_2SO_4).

(*a*) The build-up of oxygen overpotential with time is analogous to that of the hydrogen overpotential and is qualitatively similar in aqueous

H *

and non-aqueous systems, but equilibrium is attained more quickly in the latter, the average time for the attainment of approximate constancy being about 90 min.* (cf. Hickling and Salt,[14]).

(*b*) In all cases the oxygen overpotential on smooth platinum is greater in the aqueous—non-aqueous media than in water. The increment with percentage of non-aqueous component is approximately constant with increasing c.d. so that it is unlikely that there is a notable contribution from resistance error to this result.

(*c*) The Tafel equation is applicable in all systems at the lower c.d. Slight negative deviations exist in aqueous and aqueous-dioxan solutions. The slopes of the overpotential/log c.d. curves are increased by the presence of either non-aqueous component but their general shapes remain the same.

(*d*) Compared with the results for the variation of hydrogen overpotential on nickel in acetic acid-water and dioxan-water mixtures,[6] the effects of the solvent is similar up to about 50 % non-aqueous content. Whereas the hydrogen overpotential thereafter begins to decrease with further increasing non-aqueous contents, the oxygen overpotential increases slightly upon further addition of acetic acid or dioxan.

(*e*) The results do not support the quantum mechanical theory of oxygen overpotential[3] because, according to this, the overpotential should be either independent of the solvent or dependent, during variation of the solvent medium, primarily upon the solvation energy of the hydroxyl ion, according as to whether Gurney's " interphase potential " is taken to mean the metal-solution potential difference at the working anode, or the anodic overpotential. The alteration of the solvent effect with c.d., clearly marked for acetic acid systems, does not support a simple dependence on solvation energy, which probably does not differ greatly in the present systems from that in water.[16] According to Eyring, Glasstone and Laidler's view that anodic overpotentials are due to the slowness of transfer of a proton from a water molecule attached to the anode to one in solution, the effects of a non-aqueous addition appear to be due to (i) a decrease in the energy of prototropic transfer at the surface, (ii) a weakening of the force metal/proton owing to absorption of the non-aqueous component on the electrode. Both these effects would appear to indicate a decrease of overpotential upon addition of a non-aqueous component in contradiction to the results obtained.

It may be suggested tentatively that the present results lend support to the catalytic mechanism for oxygen overpotential. If it is assumed that the slow stage is the combination between atoms on the electrode surface, and that solvent molecules adhere to the surface by specific adsorptive, or electrostatic, forces, addition of acetic acid or dioxan causes replacement of some water molecules on the anode surface by the larger non-aqueous components so that the fraction of the cathode surface open for oxygen atom combination is less than before addition. Increase in overpotential, as reported here, would therefore be expected to take place, provided that no complex interactions between the adsorbed non-aqueous component and water occurred. The increase of overpotential with increasing non-aqueous content might be expected to continue until the anode surface is largely saturated with the non-aqueous component. It can be shown that this concept of adsorption of a comparatively large molecule on to the anode leads to a Tafel equation of increased slope in accord with the results.

* Foerster,[2] also observed this time variation of oxygen overpotential and found that true constancy was reached after approx. 22 hr. After 2 hr. however, the total variation only amounted to 10-20 mv. which is within the limit of reproducibility. Bowden[15] does not report any variation with time during measurements at any given c.d. and it does not seem clear from his papers at what time after the commencement of polarisation at a given c.d. were the measurements of overpotential made.

The author wishes to give sincere thanks to Dr. H. J. T. Ellingham for his interest in this work.

Summary.

1. The oxygen overpotential on smooth platinum has been measured at current densities between 10^{-8} and 10^{-1} amp./sq. cm. in M. H_2SO_4 solutions in acetic acid-water and dioxan-water mixtures at room temperatures.

2. Addition of either non-aqueous component causes the overpotential to increase rapidly at first and then more slowly, towards an apparent maximum in the case of the dioxan system, this behaviour being the same at all c.ds. within the range examined. The slopes of the Tafel lines are increased by the presence of either non-aqueous component, being approximately doubled in the presence of acetic acid. Time affects are qualitatively independent of the solvent.

3. The results do not find direct interpretation on the slow discharge or reaction-rate theories of overpotential. A catalytic mechanism is suggested.

Résumé.

(1) Le survoltage d'oxygène sur le platine poli a été mesuré à des densités de courant de 10^{-8} à 10^{-1} amp./cm.^{2} dans des solutions molaires de SO_4H_2 dans des mélanges acide acétique-eau et dioxane-eau à la température ordinaire.

(2) L'addition de chacun des composés non aqueux provoque un accroissement du survoltage, rapide au début, puis plus lent, vers un maximum apparent dans le cas du système dioxane ; l'allure du phénomène reste la même pour toutes les densités de courant dans la gamme examinée. Les pentes des lignes de Tafel sont accrues par la présence de chacun des composés non aqueux et sont approximativement doublées par l'acide acétique. Qualitativement, l'effet du temps ne dépend pas du solvant.

(3) Les résultats ne peuvent être interprétés directement d'après les théories du survoltage fondées sur la décharge lente ou sur la vitesse de réaction. Un mécanisme catalytique est suggéré.

Zusammenfassung.

(1) Die Sauerstoffüberspannung an blanken Platinelektroden in 2 norm. Lösungen von Schwefelsäure in Essigsäure—Wasser und Dioxan—Wasser Gemischen wurde bei Stromdichten zwischen 10^{-8} und 10^{-1} A/cm.^{2} und bei Zimmertemperatur gemessen.

(2) Die Hinzufügung des nichtwässerigen Bestandteils dieser Lösungsmittelgemische ruft einen zunächst raschen und dann langsamer werdenden Zuwachs der Überspannung hervor. Bei den Dioxangemischen tritt dabei bei allen untersuchten Stromdichten ein Maximum auf. Die Gegenwart des nichtwässerigen Lösungsmittels vergrössert die Steigung der Tafel'schen Linien; ungefähr zweifach im Fall von Essigsäure. Der zeitliche Verlauf der Vorgänge ist im grossen und ganzen unabhängig vom Lösungsmittel.

(3) Die Ergebnisse können nicht direkt durch die Theorie der langsamen Abscheidung oder die Reaktionsgeschwindigkeitstheorie der Überspannung erklärt werden und es wird ein katalytischer Mechanismus vorgeschlagen.

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OXYGEN OVERVOLTAGE.

PART I. THE INFLUENCE OF ELECTRODE MATERIAL, CURRENT DENSITY, AND TIME IN AQUEOUS SOLUTION.

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Although a number of measurements of oxygen overvoltage have been made,[1] there exists no comprehensive set of generally acceptable values and the dependence of the overvoltage upon experimental variables is somewhat obscure.[2] This unsatisfactory position, which prevents any useful consideration of the mechanism of the anodic evolution of oxygen, seems to be due to the difficulty of obtaining reproducible results in the measurement of oxygen overvoltage, and in particular to the marked variation of the potential with time of polarisation which has been commented upon by many workers.[3] In the present investigation a thorough survey has been made of the conditions necessary to obtain reproducible oxygen overvoltage measurements, and an experimental method has been developed which gives reliable values. This method has been applied to study the behaviour of twelve different anode materials in alkaline solution over the current density (c.d.) range 10^{-5} to 1 amp./sq. cm., and the magnitude of the oxygen overvoltage in each case and its dependence upon the nature of the electrode material, upon c.d., and upon time have been determined.

Experimental.

General Conditions.

Electrolyte.—The choice of electrolyte was governed by the following considerations: to permit the use of a wide variety of metals as anodes, an alkaline electrolyte in which they would readily become passive was mecessary; further it was desirable that it should be a good conductor to minimise resistance errors and heating effects at high currents; finally to limit the possibilities of anodic reactions it was considered that the hydroxyl ion should be the main anion present, and its concentration should be adequate to minimise any concentration polarisation effects. N. potassium hydroxide solution satisfied these conditions and was adopted as the general electrolyte to be used.

Reference Electrode.—The potential of the reference electrode relative to the theoretical reversible oxygen potential had to be known with accuracy, and to avoid liquid-junction potentials it was desirable that it should be set up in the main electrolyte used. The hydrogen electrode

[1] Coehn and Osaka, *Z. anorg. Chem.*, 1903, **34**, 86; Foerster and Piguet, *Z. Elektrochem.*, 1904, **10**, 714; Westhaver, *Z. physik. Chem.*, 1905, **51**, 65; Newbery, *J. Chem. Soc.*, 1916, **109**, 1066; Knobel, Caplan and Eiseman, *Trans. Electrochem. Soc.*, 1923, **43**, 55; Onoda, *J. Chem. Soc. Japan*, 1922, **43**, 782; *Z. anorg. Chem.*, 1927, **165**, 79; Bowden, *Proc. Roy. Soc. A*, 1929, **126**, 107; Thompson and Kaye, *Trans. Electrochem. Soc.*, 1931, **60**, 229; Hoar, *Proc. Roy. Soc. A*, 1933, **142**, 628; Garrison and Lilly, *Trans. Electrochem. Soc.*, 1934, **65**, 275; Roiter and Yampolskaya, *J. Physic. Chem. U.S.S.R.*, 1937, **9**, 763; Grube and Gaup, *Z. Elektrochem.*, 1939, **45**, 290; Thompson and Sistare, *Trans. Electrochem. Soc.*, 1940, **78**, 259.

[2] Cf. Glasstone, *Electrochemistry of Solutions* (1937), p. 492; Bowden and Agar, *Ann. Reports*, 1938, **35**, 101.

[3] Cf. Foerster and Piguet, *loc. cit.*[1]; Foerster, *Z. physik. Chem.*, 1909, **69**, 236; Westhaver, *loc. cit.*[1]; Picheta, *J. Gen. Chem. U.S.S.R.*, 1931, **1**, 377.

fulfilled these requirements and was therefore employed. The e.m.f. of the hydrogen-oxygen cell was taken to be 1·23 v. at 20° c., and this value used in calculating the oxygen overvoltages.

Preliminary Investigation.—To determine the best conditions for the measurement of oxygen overvoltage, an extensive series of observations was made using platinum and nickel anodes in N. KOH saturated with oxygen, and employing a simple potentiometer circuit. Both sheet and wire anodes were used of areas varying from 0·1 to 10 sq. cm., and with nickel the electrodeposited metal was also studied; various methods of cleaning and treatment prior to use were investigated. From these observations the following points emerged.

(*a*) The potential of the polarised anode tended to increase considerably with time of polarisation, but in general a steady value was attained after a sufficient length of time; this value was reasonably constant (changing by less than 0·01 v. in 30 min.) and in separate experiments, starting with freshly prepared electrodes, was fairly reproducible.

(*b*) Relatively mild cleaning of the electrodes in acid solutions, such that any surface oxides were removed without the underlying metal being attacked, gave the most reproducible results; heat treatment was definitely unfavourable.

(*c*) With nickel, the electrodeposited metal, plated under standard conditions on to platinum, gave rather more reproducible results than different specimens of the massive metal, although the values were of the same general order.

(*d*) With electrodes of different areas at the same c.d. the values were reasonably consistent, any variation being not more than might be expected owing to non-uniform current distribution at the largest electrodes, showing that area is itself without fundamental influence.

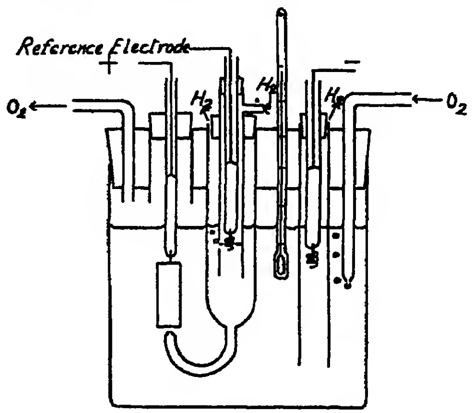

FIG. 1.—Electrolytic cell.

(*e*) At the highest c.d. of 1 amp./sq. cm. the overvoltages seemed abnormally high compared with those obtained at lower c.d.'s, and were also unsteady, suggesting that some resistance error was being included in the direct method of measurement used.

In the light of these observations the following conditions were chosen for the systematic investigation.

The Cell.—A diagram of the cell finally adopted is shown in Fig. 1. It consisted of a squat glass jar (2½ in. diam.) of about 300 ml. capacity fitted with a rubber bung which carried the various components. These comprised an inlet and outlet tube for oxygen which was bubbled continuously through the anolyte producing a measure of stirring; a thermometer; the cathode compartment which was an open-ended glass tube enclosing a 1 sq. cm. platinum wire spiral cathode; a short length of wide glass tubing in which the anode was mounted independently so that it could readily be removed without dismantling the cell; and a hydrogen electrode of the Hildebrand type which was enclosed in an outer jacket drawn out into a tube which was bent so that its capillary tip just touched the bottom edge of the anode used. The oxygen which was bubbled throuhg the anolyte and the hydrogen for the reference electrode were obtained by the electrolysis of 20 % NaOH in an electrolytic generator

fitted with Monel metal electrodes, and were washed with N. KOH before introduction into the cell; trial experiments in which hydrogen was bubbled vigorously around a working anode (polarised at a low c.d. so that the effect might be expected to be large) showed that the potential was unaffected, so that any hydrogen reaching the anode from the cathode or reference electrode by dissolution in the anolyte could be taken to have no effect. The cell was mounted in a bath of paraffin oil and was surrounded by a glass spiral through which water was circulated from a thermostat maintained at 20° C.; all observations were made with the anolyte at a temperature of 20 $\pm$ 1° C. The electrolyte was made up from A.R. KOH and 275 ml. used in the cell; it was changed in all cases before using a different anode.

Anodes.—The following anode materials have been used: Pt, Pd, graphite, Ag, Cu, Au, Fe, Co, Ni, Pb, Cd, and platinised Pt. Of these, Pt, Pd, and graphite were used in the massive form, and the remainder in the form of thin coatings electrodeposited on platinum; the graphite electrodes were machined from a block of good quality Acheson graphite. Two sizes of electrode have been used with each material of areas 0·1 and 10 sq. cm. respectively; the convenient current range with the electrical circuit employed (vide infra) was 10^{-4} to 10^{-1} amp., which permitted observations to be made with the large electrodes at c.d.'s of 10^{-5} to 10^{-2} amp./sq. cm., and with the small electrodes at c.d.'s of 10^{-3} to 1 amp./sq. cm. The smooth Pt electrodes were sealed directly into glass tubes with the requisite areas exposed; the electrodeposited metals were plated under standard conditions on to the Pt electrodes (in some cases after previous Cu plating) to form smooth coatings (except for platinised Pt) approximately 0·0005 in. thick which were microscopically examined for completeness before use. The Pd and graphite electrodes were sealed into glass tubes so as to expose the appropriate areas using "Alkathene" as a sealing material. After use the anodes were cleaned in acid solutions and thoroughly washed with water; the acid treatments adopted were as follows: Pt and platinised Pt—hot 10 N. HCl (with platinised Pt this was preceded by cathodic polarisation which experience showed was necessary to restore the metal to its original condition); Cu, Au, Ni, Co, and Ag—cold 2 N. HCl (with Ag the electrode was first washed with 2 N. NH_4OH); Pd—cold 2 N. H_2SO_4; Pb, Cd, and Fe—cold 2 N. CH_3COOH; the graphite anodes were cleaned merely by long standing in distilled water. The electroplated anodes were stripped and replated as soon as the surfaces showed signs of deterioration.

Electrical Circuit.—To avoid the possibility of resistance errors and to obtain information about the decay of oxygen overvoltage, the interrupter method [4] of potential measurement was used. The electrical circuit was fundamentally the same as that previously used in the study of hydrogen overvoltage.[5] In the present instance the interrupter was supplied with current from a 120 V. accumulator battery, the current being varied at will between 0 and 0·1 amp. by means of a Variac transformer which controlled the filament heating current of the interrupter valves. The interrupter provided usable current interruptions of between 4×10^{-5} and 20×10^{-2} sec., and was normally operated at between 1 and 5 interruptions per sec. The maximum and minimum potentials were measured in the usual way with the thyratron potentiometer-voltmeter circuit to the nearest 0·01 V.

General Experimental Procedure.—After the electrolyte had been brought to the correct temperature and saturated with oxygen, and the hydrogen electrode had been checked against a saturated calomel electrode, the freshly cleaned anode was introduced and its static potential measured with no current flowing; this served as a check of the virgin state of the anode. The polarising current was then started and a further observation

[4] Hickling, *Trans. Faraday Soc.*, 1937, **33**, 1540.
[5] Hickling and Salt, *ibid.*, 1940, **36**, 1226; 1941, **37**, 450.

made after about 1 min. had elapsed. The interrupter was then switchep on, set at a time of interruption of $8 \cdot 2 \times 10^{-5}$ sec., and observations of the maximum and minimum potentials made at frequent intervals until the latter became steady, the polarising current being kept constant throughout.[6] When this point was reached the following measurements of anode potential were made: (*a*) the full anode potential by the direct methoa without the interrupter functioning, (*b*) its maximum value with the interrupter working which was, as expected, usually identical with (*a*), ano (*c*) the minimum potentials with interruptions of 4·1, 8·2, 16, 33, 49, 66 and 82×10^{-5} sec., these being then extrapolated graphically to give the potential at zero time of interruption. Polarisation was then continued for a further 30 min., and the observations again repeated; if the change of potential in this time was less than 0·01 v. it was considered that the electrode had reached a satisfactorily steady state. A full observation o. the decay of oxygen overvoltage over periods up to 100 sec. was then made; [7] times up to 20×10^{-3} sec. were obtained using the interrupter, and for longer periods the polarising current was switched off by hand and the time taken for the potential to reach a value previously set upon the thyratron potentiometer was noted.

Observations of the overvoltage as measured by the direct method and by the extrapolation method have both been recorded in each case in the table of results (*vide infra*). Up to and including a c.d. of 10^{-2} amp./sq. cm. there was no appreciable difference between the results by the two methods, but at higher c.d.'s there seems to be no doubt that the extrapolated values are the more correct and have therefore been preferred; the direct values were abnormally high compared with those at lower c.d.'s (absurdly so in some cases at 1 amp./sq. cm.), and were often unsteady and poorly reproducible as compared with the extrapolated values. It should be noted that the rate of decay of oxygen overvoltage was usually comparatively slow, and little uncertainty was involved in the graphical extrapolation.

In general, observations were made consecutively at c.d.'s of 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} amp./sq. cm. with the 10 sq. cm. electrodes, and at c.ds. of 10^{-3}, 10^{-2}, 10^{-1}, and 1 amp./sq. cm. with the 0·1 sq. cm. electrodes, each c.d. being used in a completely separate and independent polarisation of a freshly cleaned anode. Intermediate c.d.'s were used also where necessary to define the shapes of the overvoltage—log c.d. graphs. The agreement between the values at the same c.d. with different sized electrodes was good, indicating the reliability of the method, and a mean was taken in recording the results. After each series of experiments, duplicate runs were made with freshly prepared anodes at the lowest and highest c.d.'s, and the agreement with the previous results used to give an estimate of the reproducibility of the overvoltage measurements with any one anode material.

Results.

Influence of Electrode Material and c.d.—In Table I are summarised the oxygen overvoltage values at the six standard c.d.'s for the twelve anode materials used, the latter being arranged alphabetically. The results corresponding to Method E are the extrapolated values which are judged to be the more correct and are used in all subsequent discussion; the results corresponding to Method D are the values obtained by the direct method of potential measurement and are inserted for comparison. In a few cases at very low c.d.'s it was impossible to set up an oxygen overvoltage without prior polarisation at a higher c.d. and where this has been done the

[6] It was convenient practically to keep the interrupter operating at a short period of interruption throughout the polarisation, and check experiments showed that this had no effect upon the variation of overvoltage with time, or the time required to reach a steady.state.

[7] A full account of the decay of oxygen overvoltage will be published in a later paper.

results are marked by an asterisk. With copper and silver at low c.d.'s, the anodes gave some evidence of reaching pseudo-stationary states prior to the values ultimately obtained on prolonged polarisation, and the overvoltages corresponding to thsee are inserted in brackets. In Fig. 2 the

TABLE I

Oxygen Overvoltages (v.).

Electrode Material.	c.d. amp./sq. cm. / Method.	10^{-5}.	10^{-4}.	10^{-3}.	10^{-2}.	10^{-1}.	1.	Reproducibility.
Cadmium .	E	—	0·67	0·80	0·96	1·21	1·21	±0·02
	D	—	0·67	0·81	0·97	1·27	2·50	
Cobalt . .	E	0·27	0·32	0·39	0·46	0·54	0·61	±0·01
	D	0·27	0·32	0·39	0·46	0·54	0·83	
Copper .	E	0·32*	(0·34)* 0·49*	(0·42) 0·58	0·66	0·73	0·77	±0·01
	D	0·33*	(0·34)* 0·50*	(0·43) 0·59	0·67	0·77	1·02	
Gold . .	E	0·73	0·93	0·96	1·05	1·53	1·63	±0·01
	D	0·73	0·93	0·97	1·06	1·58	2·89	
Graphite .	E	0·31	0·37	0·50	0·96	1·12	2·20	±0·03
	D	0·31	0·37	0·50	0·98	1·17	ca. 20	
Iron . .	E	0·35	0·37	0·41	0·48	0·56	0·63	±0·01
	D	0·35	0·37	0·41	0·49	0·57	0·92	
Lead . .	E	—	—	0·80*	0·97	1·02	1·04	±0·03
	D	—	—	0·80*	0·97	1·04	1·35	
Nickel . .	E	0·32	0·45	0·60	0·75	0·91	1·04	±0·02
	D	0·33	0·46	0·61	0·76	0·93	1·24	
Palladium .	E	0·39	0·48	0·89	1·01	1·12	1·28	±0·02
	D	0·39	0·48	0·89	1·02	1·15	1·72	
Platinum .	E	0·52	0·80	1·11	1·32	1·50	1·55	±0·01
	D	0·52	0·80	1·11	1·33	1·56	2·02	
Platinised platinum .	E	0·21	0·32	0·46	0·66	0·89	1·14	±0·01
	D	0·21	0·32	0·46	0·66	0·90	1·43	
Silver . .	E	(0·00) (0·20)* 0·41*	(0·01) (0·28) 0·45	(0·24) 0·60	0·71	0·94	1·06	±0·03
	D	(0·00) (0·20)* 0·41*	(0·02) (0·29) 0·46	(0·27) 0·62	0·77	1·05	1·99	

results are graphically represented by plotting overvoltage against $\log_{10}$ c.d., numerous overvoltage determinations at intermediate c.d.'s having been made where necessary to define the shapes of the curves. The dotted sections in the curves represent the joining up of points which were obtained after prepolarisation at higher c.d.'s

Of the anodes used, Ni, Fe, Pt and platinised Pt suffered no appreciable

attack and were substantially unchanged in appearance after polarisation; with Co a dark brown deposit formed on the anode at all c.d.'s. Gold was unchanged in appearance on polarisation at low c.d.'s, but at 2×10^{-2} amp./sq. cm. and higher values the anode developed a reddish-brown appearance. With Pd there was no change in the appearance of the

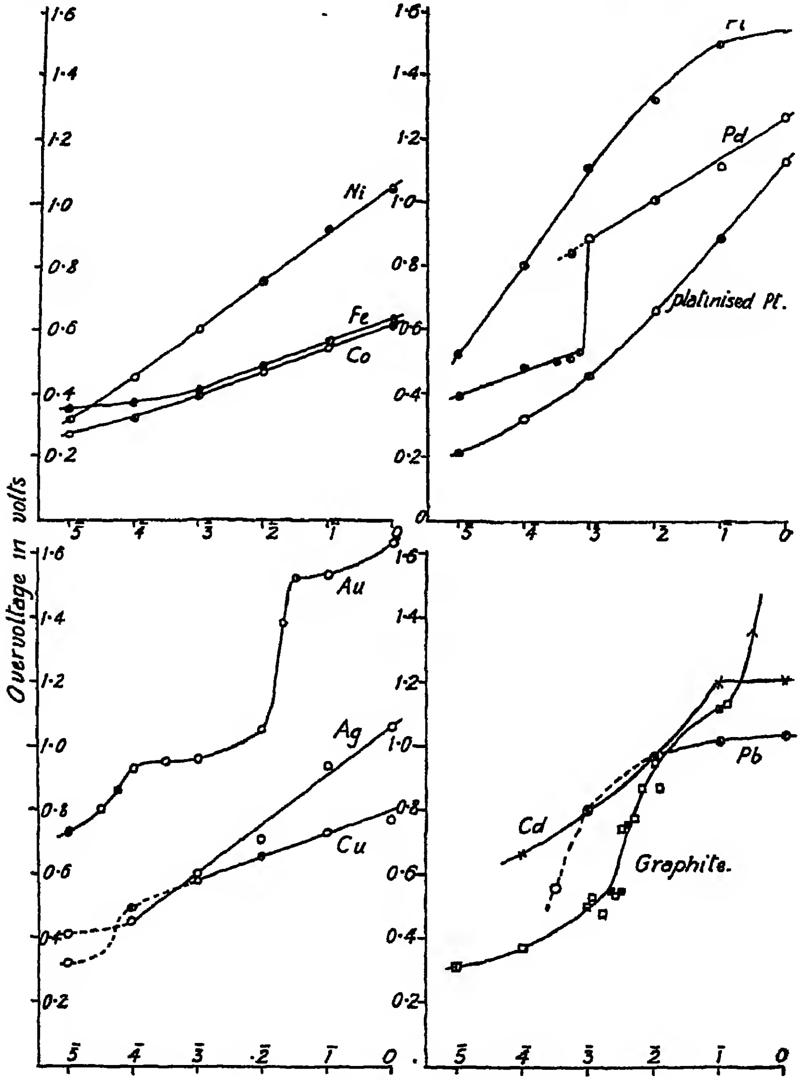

FIG. 2.—Overvoltage—log c.d. graphs.

anode at c.d.'s lower than 10^{-3} amp./sq. cm., but at higher values a golden-brown deposit formed on the surface. Graphite suffered no appreciable attack at low c.d.'s. but at 10^{-1} amp./sq. cm. and higher values the surface became badly pitted and the electrolyte was found to have an abnormally high carbonate content. At very low c.d.'s Cu became coated with a black deposit which generally disappeared on prolonged polarisation, the anode

then appearing reddish-brown; it was observed that some copper entered the solution and was deposited at the cathode. Ag became covered with a greyish-black deposit at all c.d.'s; and at high c.d.'s some silver dissolved in the electrolyte. The Cd anode was severely attacked on polarisation; the surface was progressively oxidised (colour changes of brown to greyish-green to yellow), and the oxide coatings tended to peel away exposing the metal to fresh attack; no value for the overvoltage at 10^{-5} amp./sq. cm. could be obtained. The Pb anode was also severely attacked and at low c.d.'s merely dissolved; at 10^{-3} amp./sq. cm. and higher values a brown coating formed on the electrode; this took place in two stages following

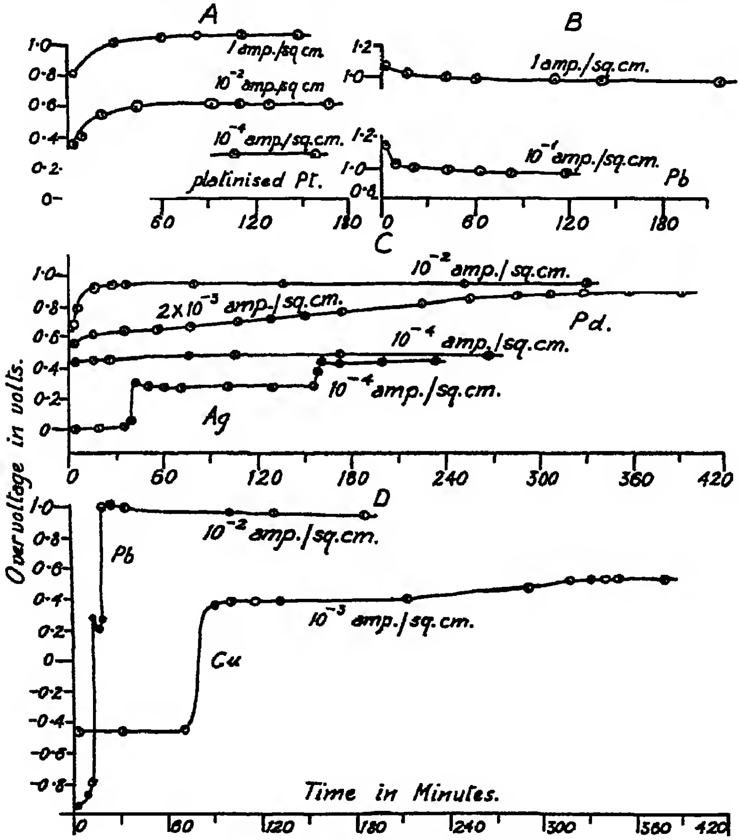

FIG. 3.—Overvoltage—time graphs.

rapidly on one another and corresponding to the two stages in the rapid potential rise shown in the overvoltage-time graph (see Fig. 3*d*).

Influence of Time.—Graphs of overvoltage plotted against time of polarisation were obtained for every anode material at each c.d. From these four different types of behaviour could be distinguished.

(*a*) The most common behaviour was that the overvoltage rose from the start of polarisation, at first rapidly and then more slowly, until it ultimately approached a steady value. The time taken to reach constancy varied widely in different cases, between about 30 min. to 4 hours, and was in general greater the lower the c.d. A typical example is illustrated in Fig. 3*a*, in which overvoltage-time curves for platinised Pt at c.d.'s of 10^{-4}, 10^{-2}, and 1 amp./sq. cm. are shown.

(*b*) A much less frequent behaviour was that the overvoltage was initially higher than the final value to which it decreased in a short time. This phenomenon was particularly shown by Pb and is illustrated in Fig. 3*b*, in which the polarisation curves at 10^{-1} and 1 amp./sq. cm. are shown.

(*c*) Where an electrode could manifest more than one overvoltage state, e.g. passed suddenly to a much higher overvoltage at a particular c.d. (cf. Pd and Au), then at c.d.'s in the region of the critical value the variation of overvoltage with time was very prolonged. This is shown in Fig. 3*c* by the graphs for Pd at c.d.'s of 10^{-4}, 2×10^{-3}, and 10^{-2} amp./sq. cm.; at the first and last of these c.d.'s the behaviour with time is quite normal and falls into category (*a*), but at the middle c.d. the variation of overvoltage with time is very prolonged and some 5-6 hours are required for a steady value to be attained. With Ag and Cu at low c.d.'s a somewhat similar phenomenon was displayed in which the ultimate steady overvoltage was preceded by one or more pseudo-steady values; this is illustrated in Fig. 3*c* by a graph for Ag at 10^{-4} amp./sq. cm.

(*d*) Where the electrode was one which was attacked and dissolved the potential was initially very negative, no oxygen overvoltage being manifest but after a time passivity usually set in and the anodic behaviour then fell into one of the previous categories; this is shown in Fig. 3*d* by the graphs for Pb at 10^{-2} amp./sq. cm. and Cu at 10^{-3} amp./sq. cm.

Discussion.

The results summarised in Table I and graphed in Fig. 2 show that the oxygen overvoltages at the anode materials studied are very substantial, and in general they are appreciably higher than corresponding hydrogen overvoltages. At 10^{-6} amp./sq. cm. no electrode shows a genuine overvoltage of less than 0·2 v., and at 1 amp./sq. cm. the overvoltages of all electrodes except Co, Fe and Cu are well over 1·0 v. and at Au, graphite and Pt reach very high values indeed. The dependence of overvoltage on c.d. varies so greatly with the different electrode materials that it is impossible to arrange them in any order of increasing or decreasing overvoltage which will be generally valid. On the whole Co, Fe and Cu display relatively low overvoltages while those of Pt and Au are high; the position of the other electrode materials in the series depends very largely on the c.d. at which measurements are made. It may be noted that if allowance is made for the fact that the real surface area of platinised Pt is very much larger than that of smooth Pt (probably of the order of 1000 times), these two materials do not seem to differ appreciably in their behaviour as regards oxygen overvoltage.

It seems to have been generally assumed that the dependence of oxygen overvoltage (η) on c.d. (I) is in accordance with Tafel's equation

$$\eta = a + b \log I,$$

where a and b are constants, and it has even been suggested that in acid solution b has the same value as for hydrogen overvoltage.[8] This conclusion appears to have been reached from the results of a very few experiments in which platinum has been the sole anode material used over very limited ranges of c.d. and in which the importance of the time factor (*vide infra*) has been ignored. The present results, as shown in Fig. 2, reveal a much more complicated state of affairs. Over limited ranges of c.d., the graphs for Co, Fe, Ni, Pt, platinised Pt, Pd, Ag and Cu all show agreement with an equation of the Tafel type, but when the graphs are considered in their entirety a number of divergences are apparent. Thus at very low c.d.'s, there appears to be a general tendency for the overvoltages to approach constant minimum values; this is clearly shown in the graphs for Co, Fe, platinised Pt and Ag, and the same tendency can be

[8] Cf. Bowden and Agar, *Ann. Reports*, 1938, 35, 101.

detected in other cases. At high c.d.'s, the graph for Pt also shows a tendency to approach a constant maximum value. The most striking feature, however, is the stepwise nature of certain of the graphs. Thus at a c.d. of approx. 10^{-3} amp./sq. cm. the overvoltage at Pd changes abruptly by nearly 0·4 v., and the η-log I graph appears as two approximately straight lines joined by an almost vertical section; there appeared to be some slight hysteresis in the change since after prepolarisation at higher c.d.'s the upper section of the graph could be slightly extended in the direction of decreasing c.d. With Au the η-log I graph had the remarkable form shown in Fig. 2 and was quite reproducible; no part of the graph seems to follow a Tafel equation, and at c.d.'s rather greater than 10^{-2} amp./sq. cm. there is a steep rise of overvoltage of about 0·5 v., it being possible in this case actually to obtain points on the steep section of the curve. Graphite gave a curve of a somewhat similar type; the reproducibility of the overvoltage measurements was poorer here than at the other anode materials studied, but very numerous observations were made and these leave no doubt as to the general form of the graph. Ag and Cu electrodes also showed signs of a stepwise variation of overvoltage with c.d. but in these cases at very low c.d.'s; thus from Table I it may be seen that several values of overvoltage could be obtained according to time of polarisation and the pretreatment of the anodes. It seems most likely that these sudden changes of overvoltage with c.d. are associated with changes in the surfaces of the anodes; thus, as already noted in the experimental section, with Pd at c.d.'s higher than 10^{-3} amp./sq. cm. a golden-brown deposit formed on the surface of the anode, while with Au at 2×10^{-2} amp./sq. cm. and higher c.d.'s the anode developed a reddish-brown appearance. For completeness the graphs for Pb and Cd are included in Fig. 2, but it is very doubtful what significance can be attached to them, since both these anodes were severely attacked during use.

It must be concluded, therefore, that the Tafel equation $\eta = a + b \log I$ has only a limited application to oxygen overvoltages in alkaline solution and is far from giving an adequate description of the dependence of overvoltage upon c.d. In the cases where it does apply it is of some interest to evaluate the constant b, and from the present experiments the following results are obtained:

Fe 0·07, Co 0·07, Cu 0·07, Pd (low c.d.'s) 0·08, Pd (high c.d.'s) 0·13, Ni 0·15, Ag 0·15, platinised Pt 0·24, Pt 0·30.

It should be noted that none of these values is in close agreement with or shows any simple relation to the quantity $2{\cdot}302 \times 2RT/F$, i.e. 0·12 at 20° c., which some workers consider of fundamental importance in connection with b.

The present work has shown that in practically all cases a considerable period of polarisation at constant c.d. is required for a steady value of oxygen overvoltage to be reached. The importance of this factor in determining the conditions necessary for satisfactory measurements of oxygen overvoltage cannot be too greatly emphasised, but almost without exception it has been consistently ignored by previous workers and this has no doubt greatly contributed to what appears to be a general belief that it is extremely difficult to obtain reproducible values for oxygen overvoltage. Thus, in the method of measurement which appears to have been generally adopted, observations of potential have been made at a series of increasing or decreasing c.d.'s, the time of polarisation at each c.d. being either left quite indefinite or fixed at some arbitrary period.[9] This

[9] Thus Knobel, Caplan and Eiseman (*Trans. Electrochem. Soc.*, 1923, 43, 55) made a fairly extensive survey of oxygen overvoltages at several electrodes in N. KOH over fairly wide c.d. ranges; they used the direct method of measurement and measured the potentials at a series of ascending c.d.'s, *an arbitrary time of 1 min. being allowed at each c.d.* Comparison of their results with those obtained in the present investigation shows that where conditions are such that the over-

procedure is completely unsatisfactory in that the state of polarisation of the electrode is changing progressively with time throughout the series of measurements, and any overvoltages so determined are characteristic neither of a virgin anode nor of a fully polarised anode, nor can the values at different c.d.'s be fairly compared with one another. On the other hand, the procedure adopted in the present investigation, in which a virgin anode is used at every c.d. and polarised until a steady potential is reached, has given uniformly satisfactory results, although it is very laborious and time consuming; as indicated in Table I, the results are very closely reproducible.

It is not desired at this stage to advance any general theory of the mechanism of oxygen overvoltage; until the effects of other variable factors such as concentration and nature of electrolyte, hydrogen ion concentration, temperature, etc., which are at present under investigation, have been determined, any attempts at speculation seem to the present authors to be premature.

One of the authors (S. H.) gratefully acknowledges financial assistance received from Peter Spence and Sons Ltd. during the course of this work.

Summary.

1. Oxygen overvoltage measurements have been made in the c.d. range 10^{-5} to 1 amp./sq. cm. for twelve anode materials in an aqueous solution of N. KOH by an experimental method which gives closely reproducible results.

2. In nearly all cases appreciable time is required for overvoltage equilibrium to be set up, and the importance of this factor in determining the conditions for satisfactory overvoltage measurements to be made is emphasised.

3. Oxygen overvoltages at all the anodes studied are substantial and in general higher than the corresponding hydrogen overvoltages. The dependence of overvoltage upon c.d. varies so greatly at the different anodes that it is not possible to arrange them in an order of increasing or decreasing overvoltage which will be generally valid.

4. Over limited ranges of c.d. Tafel's equation applies to certain of the anodes, the factor b varying between 0·07 and 0·3 at different electrodes, but it is inadequate as a general description of the dependence of overvoltage upon c.d. Some anodes show no agreement with the equation, and even where it is approximately obeyed there are discrepancies at low and high c.d.'s

5. With certain anodes, notably palladium, gold and graphite, sudden changes of overvoltage occur in critical c.d. regions.

Résumé.

Le survoltage d'oxygène pour 12 anodes en différentes matières dans une solution aqueuse normale de KOH a été mesuré de façon reproductible avec des densités de courant allant de 10^{-5} à 1 amp./cm.^{2}. Le survoltage d'oxygène est en général supérieur à celui d'hydrogène et la valeur d'équilibre est atteinte lentement. En tant que description générale du survoltage en fonction de la densité de courant, l'équation de Tafel se révèle inadéquate, bien qu'elle puisse être appliquée à certaines anodes dans un domaine limité de densité de courant. On note des changements brusques de survoltage dans des régions critiques de la densité de courant, notamment pour les anodes en Pd, Au et graphite.

voltages do not vary very greatly with time the agreement is reasonably good, but in other cases their values are widely different from the final steady values reached in the present work. It is of interest to note that their values for Au indicate a dependence upon c.d. similar to that now found, although they do not comment specially upon this.

Zusammenfassung.

Reproduzierbare Messungen der Sauerstoffüberspannung an zwölf verschiedenen Anodensubstanzen in wässeriger norm. KOH bei Stromdichten von 10^{-3} bis 1 A/cm² werden berichtet. Im allgemeinen ist die Sauerstoffüberspannung, deren Gleichgewichtswert nur langsam erreicht wird, höher als die Wasserstoffüberspannung derselben Elektrode unter den gleichen Umständen. Tafel's Gleichung für die Beziehung zwischen Überspannung und Stromdichte wurde als unzureichend gefunden, obzwar sie für bestimmte Anoden in einem beschränkten Stromdichtenbereich gültig ist. Bei bestimmten kritischen Stromdichten wurden plötzliche Veränderungen der Überspannung beobachtet, besonders für Anoden aus Pd, Au und Graphit.

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THE ENERGY OF ACTIVATION IN THE ELECTRODEPOSITION OF OXYGEN.

By H. P. Stout

Received 21st February, 1947

The electrodeposition of oxygen at platinum anodes has been investigated in acid solution by Bowden [1] and in alkaline solution by Hoar.[2] In both cases the kinetics of the reaction conformed to the usual equation for activation overpotential,

$$\eta = \text{const.} + 2\cdot3 \frac{RT}{\alpha F} \log i$$

where η and i are the overpotential and the current density respectively, and α is a constant.

In acid solution α is equal to 0·5 and is independent of p_H, but in alkaline solution the value is generally higher and Bowden and Keenan [3] have found that it increases steadily with increasing p_H, becoming as great as 1.7 in 14 N. NaOH. This difference suggests that the rate-determinng process is different in acid and alkaline solution, in which case it would be expected that the energies of activation at the reversible potentials would be different in the two solutions. The energy of activation for deposition on platinum from N./5 sulphuric acid is 18·7 kcal. at the reversible potential of 0·9 v. against a saturated calomel electrode (S.C.E.) at a temperature of 35° c.,[1] but no measurements appear to have been made for alkaline solutions.

A determination of the energy of activation for deposition on platinum from N./10 NaOH was therefore made using the method and apparatus described previously.[4] The energy of activation at constant current was there given as

$$H = -\alpha FT\left(\frac{dV}{dT}\right)_i$$

V being the electrode potential, and its evaluation requires a knowledge of $(dV/dT)_i$ and α.

The value of $(dV/dT)_i$ was obtained by alternately heating and cooling

[1] Bowden, *Proc. Roy. Soc. A.*, 1929, **126**, 107.
[2] Hoar, *ibid.*, 1933, **142**, 628.
[3] Bowden and Keenan (unpublished). See also Keenan, *Diss.* (Cambridge, 1936).
[4] Stout, *Trans. Faraday Soc.*, 1945, **41**, 64.

the electrode over a range of temperature from about 18° to 32° c., the current being held constant, and plotting the variation with time of both electrode potential and temperature. The potential was measured against a saturated calomel electrode, and the temperature by means of a thermocouple in good thermal contact with the electrode. The mean values of the potentials at 20° and 30° c. were read off from the graphs, and the mean values of dV/dT calculated over this temperature range. Table I gives the values so obtained for four different platinum electrodes. The mean value of $(dV/dT)_t$ is therefore $-2{\cdot}2^4$ mv./° c. at 25° c. and a potential of 0·64 v. against saturated calomel. The value of α was obtained from the slope of the potential-log c.d. curve at 25° c., using the same electrodes. A typical curve is shown in Fig. 1, and the mean value of α for the four electrodes was 1·0.

On inserting the above values of α and $(dV/dT)_t$ in the expression for the energy of activation, this becomes 15·4 kcal. at 25° c. and 0·64 v. against a S.C.E. The reversible potential in this solution was 0·21 v. against a S.C.E., and as it has been shown by Bowden [1] that the energy of activation varies with the electrode potential as $-\alpha\Delta VF$, ΔV being the increase in potential, it follows that this energy at the reversible potential

TABLE I

Mean Potential against S.C.E.	Temp. Coefficient of Potential at 25° c.
(v.)	(mv/°c.)
0·65	— 2·31
0·64	— 2·20
0·64	— 2·18
0·63	— 2·27

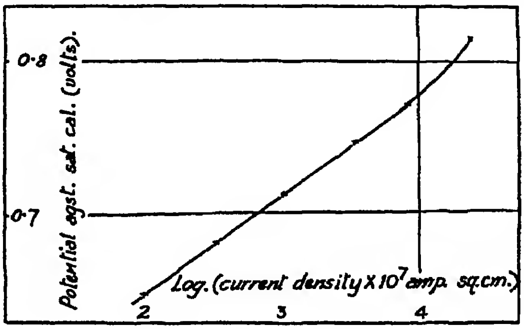

FIG. 1.

is 25·3 kcal. The energy of activation at the reversible potential in alkaline solution is thus appreciably greater than the corresponding value in acid solution, in agreement with the view that the rate-determining processes are different in the two cases.

I should like to thank Dr. F. P. Bowden for his advice and criticism, and the Chemical Society for grants for apparatus.

Resume.

Les travaux publiés sur le dépôt électrolytique de l'oxygène à des électrodes de platine, suggèrent que la réaction suit un cours différent, selon qu'elle a lieu en milieu acide ou alcalin. On pourrait s'attendre par conséquent à ce que l'énergie d'activation soit différente dans les deux cas ; c'est bien ce que montre la comparaison entre la valeur connue de 18·7 kcal. au potentiel réversible dans des solutions N/5 acides et la valeur récemment obtenue au potentiel réversible dans des solutions N/10 alcalines.

Zusammenfassung.

Veröffentlichte Arbeiten über die elektrolytische Abscheidung von Sauerstoff an Pt-Elektroden weisen darauf hin, dass die Reaktion in sauren und alkalischen Lösungen verschiedenartig verläuft, wonach zu erwarten ist, dass die Aktivierungsenergie in den zwei Fällen verschieden ist. Im Einklang damit ist diese 18·7 kcal. für das reversible Potential in 0·2 norm. Säure, wogegen jetzt gefunden wird, dass sie für das reversible Potential in 0·1 norm. Lauge 25·3 kcal. beträgt.

GENERAL DISCUSSION.

Prof. N. K. Adam (*Southampton*) said: I am not sure that the occurrence of the Kolbe or Crum Brown and Walker syntheses at an anodic potential 0·4 or 0·8 v. more positive than that required for oxygen evolution is very "anomalous". The overpotential at metallic anodes generally increases if a surface film is formed on the anode; in Fig. 3 of Hickling and Hill's paper, the potential of copper increases suddenly by about 0·9 v.; and of lead by no less than about 2·0 v., at a certain stage of oxidation. If a surface film of acetate ions were formed, sufficiently compact to prevent many hydroxyl ions reaching the anode, then these would be discharged in preference to hydroxyl ions and the Kolbe synthesis ought to take place instead of oxygen evolution; similarly strong adsorption of the half-ester ions would result in the Crum Brown and Walker synthesis. There is obviously some obstruction to the discharge of the hydroxyl ions and this would seem most easily provided by a strongly adsorbed film of the organic ions. Possibly manganese salts act by oxidising the organic ions.

Dr. D. D. Eley (*Bristol*) said: Like Prof. Adam, I would also suggest that physical adsorption of the acetate ion lies at the root of Dr. Hickling's problem. The acetate ion will be adsorbed by London forces and exclude hydroxyl ions from the electrode, an effect comparable with the raising of hydrogen overvoltage by paraffinic and other strongly adsorbed cations. Indeed, if one could find some cationic nitrogen or similar compound that would decompose on addition of an electron one might expect to find a complete parallel.

The effect of increased temperature would be to desorb the acetate ion and then to permit the discharge of hydroxyl ion. It would be interesting to know how the higher acids behave; do they show an efficiency which parallels their effect on the surface tension of water? For a complete cessation of hydroxyl discharge it would be necessary for the fatty ions to pack closely on the electrode surface and ions such as citrate, which Dr. Hickling says do not inhibit oxygen evolution, may fail in this respect.

In so far as the processes are not limited by diffusion to the electrode, we should not expect the greater rapidity of the hydroxyl ion to lead to a displacement of the adsorbed acetate layer, as mentioned by Prof. Wynne Jones.

Prof. A. R. Ubbelohde (*Belfast*) said: With regard to the paper by Hickling, a question of fundamental interest for the theory of overpotential is whether this potential refers only to the primary electron-transfer reaction, or whether it includes subsequent reactions. For example one proposed mechanism for the Kolbe reaction involves the following:

$$RCOO' \rightarrow RCOO + e + \Delta F_1 \quad . \quad . \quad . \quad . \quad (1)$$
$$RCOO \rightarrow R + CO_2 + \Delta F_2 \quad . \quad . \quad . \quad . \quad (2)$$
$$2R \rightarrow R_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is not clear whether the overpotential associated with this mechanism is related to the free energy change ΔF_1 or to $\Delta F_1 + \Delta F_2$. An alternative mechanism following (1) is

$$2RCOO \rightarrow (RCOO)_2 + \Delta F_3 \quad . \quad . \quad . \quad . \quad (2')$$
$$(RCOO)_2 + 3H_2O \rightleftarrows 2RCOOH + H_2O_2 + \Delta F_4 \quad . \quad . \quad (3')$$

and provided that the free energy changes in reactions (2′) and (3′) are to be added thermodynamically to give the resultant overpotential, it can be understood why catalysts for the decomposition of hydrogen peroxide determine the actual overpotential set up. This formation of organic peroxides may also occur from other ions prior to the hydrolysis

to hydrogen peroxide. Some incomplete experiments suggest for example

$$RO' \rightarrow RO + e$$
$$2RO \rightarrow R_2O_2,$$

where R is an alkyl radical.

Dr. T. P. Hoar (*Cambridge*) said: Hickling's description of the preferential occurrence of the Kolbe and Crum-Brown reactions rather than oxygen evolution as "anomalous" seems unnecessary. It is not in the least uncommon for a thermodynamically less easy reaction to occur more rapidly than a thermodynamically easier one; and it is certainly *not* "axiomatic" that cathodic reactions occur in "thermodynamic" order —if it were, we should call the deposition of iron and zinc from acid solutions "anomalous". *A fortiori,* the Kolbe reaction is in fact thermodynamically easier than oxygen discharge in weakly acid solutions, the respective standard potentials (E_H) being *ca.* − 0·16 [1] and + 1·23 v.

We may represent the state of affairs in a schematic potential-c.d. diagram (Fig. 1), showing $E - i$ anodic polarisation curves for oxygen discharge (curves A, A′) and for the Kolbe reaction (curves B, B′), each under conditions where the electrode process proceeds without any inhibition, i.e. at an "unpoisoned" electrode, and also under conditions of electrode poisoning. This scheme shows how the main reaction at the c.d., i, can be oxygen discharge at + 2·0 v., if the Kolbe reaction is inhibited but oxygen discharge is not; while the main reaction at the same c.d. can be the Kolbe reaction at + 2·4 v., if oxygen discharge is inhibited but the Kolbe reaction is not. It is reasonable to suppose that oxygen discharge may be inhibited by the reactants and/or intermediates and/or resultants of the Kolbe process; acetate ions, acetate radicles and CO_2 may be expected to be readily adsorbed on the electrode surface and could well poison it for oxygen discharge. Such absorbed layers, e.g. of acetate ions as suggested by Adam, would of course be in a dynamically steady state with respect to the whole system; their removal by reaction or desorption would be balanced by further deposition. The Kolbe reaction may perhaps be inhibited by anodically deposited oxides of lead, manganese, etc., that do not much alter the activity of the electrode for oxygen discharge.

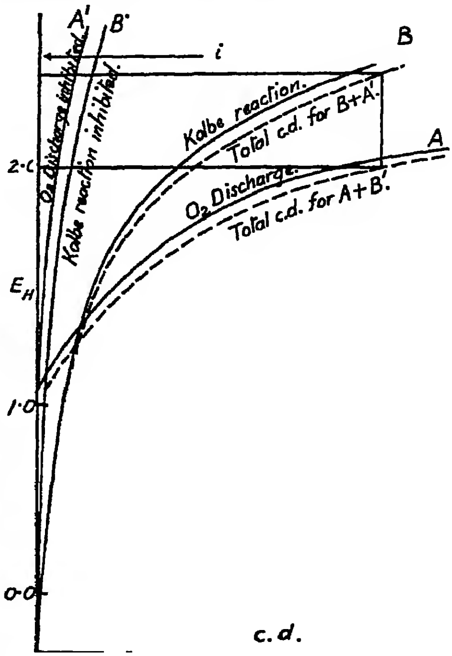

FIG. 1.

Dr. F. Wormwell (*Teddington*) said: I do not feel competent to advance any detailed constructive suggestions for explaining the apparent anomalies raised by Dr. Hickling, but I should like to mention several

[1] Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions* (1938), p. 123.

points in the hope that they might stimulate useful lines of thought. The apparent neglect of spatial factors has already been dealt with by Prof. Adam. It would seem important, even when considering electrochemical phenomena, not to overlook the importance of spatial and kinetic factors. Dr. Agar[1] has already stressed the danger of neglecting other variables than potential and current when considering the rate of an electrode reaction.

The examples given by Dr. Hickling involve the reactions of organic compounds. Is this significant, or are examples known that involve only inorganic ions of smaller size than the organic ions quoted? It would also be of interest to know whether the nature of the electrode metal, or of its surface preparation, has any influence on the reactions. In another connection, Dr. Hickling has stressed the desirability of studying anodic processes on other metals. I should also like to suggest that a study of the mechanism of the inhibiting effect of manganous ions might throw light on the mechanism of the anomalous reactions.

Dr. M. Haissinsky (*Paris*) said: The difficulties reported by Dr. Hickling in his paper on the anomalies of anodic reactions could perhaps be formulated in the following manner. Why in presence of acetate and ethylmalonate ions the oxygen overvoltage on a smooth platinum anode is, under some conditions, so large that reactions demanding very high potentials become possible? The situation is then much less dramatic and the answer to this question will perhaps be found when the effect of the addition of various substances on the oxygen overvoltage at different electrodes will be known. As Hickling stated, our experimental knowledge of the oxygen overvoltage is as yet poor and unsatisfactory. One can hope the systematic research undertaken by Dr. Hickling and his coworkers and by Dr. Bockris on this subject will help to overcome the difficulties reported.

Dr. J. N. Agar (*Cambridge*) (*communicated*): Any alteration in the potential of an electrode must be due to some change in the distribution of charged particles in the neighbourhood of the electrode-solution interface. It seems to be largely a matter of convenience whether we picture the charge distribution (or the field and potential associated with it) as controlling the reaction rate, or regard it as a steady distribution of ions and electrons established by the occurrence of the reaction at some specified rate. If the former point of view is adopted, however, the overall potential is only one of several factors that may affect the rate; as several speakers mentioned, adsorption and similar effects must be taken into account. It is worth noting that adsorption of ions or dipoles may not only block the available reaction sites but may also alter the potential gradient close to the interface, even though the overall metal-solution potential difference remains constant.

Dr. A. Hickling (*Liverpool*) said: Adam's explanation of the anomalous anode potentials observed in the electrolysis of acetate and ethyl malonate solutions is a very plausible one, but I am not sure that it accounts for all the experimental observations. I would emphasise that the high potentials are observed from the very beginning of electrolysis, so that it is not a question of a low potential process being replaced by a high potential one after a certain time. Also, at electrodes where the Kolbe and Brown-Walker syntheses do not occur the oxygen evolution potentials are quite normal and it is difficult to see why adsorbed films of organic ions should not also be present in these cases. I feel very strongly myself that the anomalies are of a more fundamental nature, and are bound up in some way with peculiarities in the discharge of hydroxyl ions.

Prof. N. K. Adam (*Southampton*) said in reply to Hickling: No, I think collateral evidence would be necessary to account for the non-existence of a strongly adsorbed film of organic ions on gold and the other anodes on which the Kolbe synthesis does not easily occur.

[1] This vol., p. 81, para. 1.

In reply to Wynne-Jones: I see no reason why, if organic ions are adsorbed *initially*, they should not continue to be adsorbed during electrolysis.

Dr. T. P. Hoar (*Cambridge*) said: Hickling and Hill demonstrate the complexity of oxygen overpotential phenomena, showing in particular that the electrode material exercises a profound influence. It is certain that in many cases the electrode surface becomes oxidised, often during the overpotential measurements, and that the so-called "inert metallic basis" for the oxygen discharge reaction is really oxide in a state of flux. Thus in the present measurements on smooth platinum, extrapolation of the straight part of the $\eta - \log_{10} i$ graph to zero overpotential gives a current at the reversible potential of *ca.* 10^{-7} amp., whereas for an apparently similar electrode I found *ca.* $10^{-12} - 10^{-13}$ amp. in both acid and alkaline solutions.[3] This large difference *may* arise because my electrodes were poisoned by absorption of impurities from Picein wax, but the electrodes were reproducible and I think this improbable; it is more likely that they were relatively less active because they were given a preliminary prolonged anodic treatment, probably converting the surface to oxide. I found this treatment absolutely necessary if reproducible overpotential results (i.e., the same $\eta - \log_{10} i$ straight line, whether determined with a series of increasing or decreasing currents) were to be obtained. Hickling and Hill do not state whether their smooth platinum electrode continued to show relatively low overpotential and high reversible current after continued anodic polarisation.

The electrode lay-out, shown in Fig. 1 of Hickling and Hill's paper, is open to the criticisms that the c.d. on the electrode will be greater at the edges than in the centre—a point made by Goodeve in this Discussion—and that the potential is measured near to the bottom edge.

Dr. A. Hickling and Mr. S. Hill (*Liverpool*) (*communicated*): With reference to the point raised by Hoar and earlier by Goodeve regarding the electrode arrangement in overvoltage measurements, it should be pointed out that in our study of oxygen overvoltage observations have been made with both 0·1 sq. cm. wire electrodes and 10 sq. cm. sheet electrodes at the same apparent current densities, and good agreement has been found. This would seem to indicate that any lack of uniformity in the c.d. at the anodes used is not such as seriously to affect the measurements.

Miss P. M. Bryant (*Bristol*) said: In connection with the experiments of Hickling and Hill on oxygen overvoltage when they observed discontinuities in the overvoltage-log c.d. curves for palladium, gold and graphite electrodes, it may be of interest to mention that I noticed a similar effect with platinised platinum electrodes in dil. HCl. At the lower c.d.'s a normal overvoltage-c.d. curve was obtained, but at a certain critical c.d. there was a sudden, very rapid increase of potential. On increasing the c.d. beyond this, the curve continued normally although displaced; repetition of the measurements at the lower c.d.'s gave a curve which was a continuation backwards of the displaced curve, and the values of potential obtained originally at the lower c.d.'s could not be repeated. This discontinuity was only observed with platinised platinum and not with any other metal used as a cathode in dil. HCl.

Dr. A. F. H. Ward (*Manchester*) said: The observation by Hickling and Hill of a time-effect in the production of overvoltage is of interest. This time-effect may be complicated since several phenomena are involved, one of which may be adsorption on the surface. It is useful to bear in mind that when adsorption on an interface takes place without any electrical or other complications a time-effect may also be shown. This slow adsorption is manifested by a variation of interfacial tension with time.[4] It is not suggested that the time-effect now observed for overvoltage is necessarily determined by a slow adsorption process. However,

[3] Hoar, *Proc. Roy. Soc. A*, 1933, **142**, 628.
[4] Ward and Tordai, *Nature*, 1944, **154**, 146.

in the development of any theory of a time-effect of overvoltage it is important to remember that it may be incorrect to assume that adsorption is necessarily a rapid process, in comparison with other accompanying phenomena.

Dr. J. O'M. Bockris (*London*) said: Considerable thanks are due to Hickling and Hill for making quite clear that the oxygen overpotential bears very little relation to the hydrogen overpotential in regard to its dependence upon c.d. The converse conclusion,[5] based upon insufficient evidence, had led to confused theorising.[6]

The use of alkathene cement for Pd and graphite anodes seems undesirable; in hydrogen overpotential measurements with platinised platinum, the present author and R. Parsons have observed a poisoning effect with alkathene cement.

No details are given in Stout's paper of the method of preparation of the electrode. However, the discrepancies in comparison with the results of Hickling and Hill are rather large ($\alpha = 1$ and 0·2) and it seems probable that this is due to the fact that Stout has not taken into account the variation of overpotential with time without which no comparable results can be obtained.

Dr. H. P. Stout (*Saltcoats*) (*communicated*): With regard to Dr. Bockris' comment that the slope of the $V-\log i$ curve for platinum given by Hickling and Hill in Fig. 2 is appreciably different from the slope of the $V-\log i$ curve in Fig. 1 of my paper, I would like to point out that on extrapolating to the reversible potential, the current in my case is about 10^{-13} amp./sq. cm. compared with 10^{-7} amp./sq. cm. for Hickling and Hill. The figure of 10^{-13} amp./sq. cm. is in good agreement with corresponding figures obtained previously by Hoar and it would appear that conditions in Hickling and Hill's experiments were entirely different from those in Hoar's and my experiments. In view of the much larger time of polarisation in the former case, it is likely that Hickling and Hill's electrodes were quite heavily oxidised.

Dr. J. O'M. Bockris (*London*) (*communicated*): The suggested explanations of Dr. Hoar and Dr. Stout for the lack of agreement of their results with those of Hickling and Hill appear to be in opposition. The discrepancy seems connected with the time variation of oxygen overpotential; measurement of a varying potential "immediately" after commencement of polarisation at a given c.d. seems a less easily reproduced condition than that of Hickling and Hill.

Dr. H. Wilman (*London*) said: In connection with Dr. Hickling's paper on some anomalies in the concept of electrode potential as the determining factor in the occurrence of anodic reactions, and his paper with Dr. Hill on oxygen overvoltage variation with anode material, c.d. and time, there are some of our electron diffraction results which seem to me to clarify the situation. Our results also lead to the conclusion, which Dr. Hickling expresses, that "the anode potential is the result of the reaction taking place, rather than the factor which determines which reaction shall occur."

Referring first to the most definite cases, Dr. Hickling and Mr. Hill observed with gold, palladium and graphite anodes a sudden increase in overvoltage at a certain stage as the c.d. is increased, and that at this stage the gold became reddish-brown and the palladium golden-brown, while at rather higher c.d. the graphite showed appreciable pitting and attack, forming carbonates in the electrolyte. A colour change by itself is not of course reliable evidence of compound formation in the form of a layer on the anode surface, since it is often associated with changes of physical form (surface roughness, crystal size and orientation) of a material, rather than formation of a chemically-changed surface layer. For example, smooth platinum has a high reflection for white light, but finely divided

[5] *Proc. Roy. Soc. A.*, 1929, 126 107. [6] *Ibid.*, 1931, 134, 137.

or rough platinum surfaces appear black (platinum black); and I found that silver which had been used as catalyst of an ammonia reaction appeared creamy-white and rough though the clear electron diffraction pattern showed only normal silver present. We have observed, too, that copper treated anodically at 0·1 amp./sq. cm. in 25 % HCl first turns dark grey, then white, then light grey, then yellowish-brown, though in all these stages the electron diffraction patterns showed only cuprous chloride on the surface, with some copper as well in the first stage. In the case of gold, however, Finch and Sun[7] showed that the reddish colour formed on gold in N. KCl at 0·015-0·12 amp./sq. cm. and 25° C. was due to a surface layer of a compound which they were not able to identify; and we have since prepared anodic layers showing interference colours on gold, in 10 % KOH at 0·2 amp./sq. cm. which yielded patterns due to a different compound.

Thus it seems practically certain that the colour change and sudden rise of overvoltage observed by Dr. Hickling and Dr. Hill on gold and palladium are associated with, and in fact caused by, the formation of a surface layer of some compound of the anode metal, though the nature of the compound depends on the electrolyte used. The rise in the overvoltage curve for graphite seems at first sight to lie outside this explanation, but in this case there is the possibility of a penetration of O^- ions between the (001) sheets of hexagonally-linked carbon atoms in the graphite layer lattice, amounting to a compound formation (graphitic oxide).[8]

In NaOH or KOH we have also observed brownish surface layers of $Cd(OH)_2$ formed on Cd in 10 % NaOH or KOH at 18° C. and 0·04 to 0·17 amp./sq. cm., grey films of ZnO on Zn anodes in 10 % NaOH at 0·06 amp./sq. cm., dark orange-brown layers (whitish when dry) of unknown composition on Cu in 20 % NaOH or KOH, dull greyish films on Ni in 0·25 % NaOH at 0·1 amp./sq. cm. giving very diffuse electron diffraction patterns which may have been due to NiO or $Ni(OH)_2$. In most of these cases the c.d. fell during formation of the film, and the bath voltage rose by an amount of the order of the rise found by Hickling and Hill in their experiments.

With respect to Dr. Hickling's observations on the Kolbe and Crum Brown-Walker reaction anomalies on smooth Pt, which are not observed on Pt black, this seems likely to be due to adsorption of the organic molecules side-by-side on the smooth Pt to form a close-packed layer or pseudo-crystal. We know from our electron diffraction observations that long-chain hydrocarbons and their derivatives tend to do so, and moreover that such layers usually have very smooth surfaces relative to the interatomic or intermolecular distances; and that associated with this smoothness and close packing there is a striking resistance to chemical attack. For example, a zinc cleavage face remains bright and untarnished in air almost indefinitely, whereas a rough surface quickly oxidises and tarnishes; and I have heated a zinc crystal in air to its m.p. and still the electron diffraction pattern from the cleavage face showed only zinc. In the zinc cleavage surface the atoms are in the most dense packing possible. On the atomically-rough surface of Pt black a layer of adsorbed molecules must be unable to form a continuous close-packed layer and must be correspondingly relatively readily attacked by O^- ions. It therefore seems quite reasonable to expect an overvoltage at the smooth Pt in these reactions, while little or none occurs on Pt black. If this explanation is correct the observed overvoltage should be a measure of the potential difference required to neutralise an O^- ion by attracting its extra electrons to the Pt surface through the adsorbed layer of molecules.

Dr. A. Hickling (*Liverpool*) said: With reference to oxygen overvoltage

[7] *Trans. Faraday Soc.*, 1936, **32**, 852.

[8] cf. Lowry and Bozorth, *J. Physic. Chem.*, 1928, **32**, 1524; Hofmann, *Ber.* 1932, **65**, 1821.

it is apparent that we are all at present at the stage of accumulating experimental data, and it is likely to be some considerable time before any useful theory emerges. It is therefore of the greatest importance that we should seek agreement in the results obtained by different workers, and endeavour to elucidate any discrepancies which are apparent. Now I note that Stout reports that oxygen overpotential obeys an equation of the Tafel type with b having a value of 0·12 in acid solution, this decreasing in alkaline solution, and his experimental value in 0·1 N. NaOH is approximately 0·06. This is contrary to the results found by Hill and myself. In general we find the Tafel equation to be approximately obeyed at platinum, but the value of b is greater in alkaline than in acid solution, and in N. KOH is approximately 0·30. This very considerable discrepancy is probably due, in my opinion, to the neglect of the time of polarisation factor in Stout's experiments. Oxygen overvoltage in general changes very markedly with time of polarisation, and the only way in which we have been able to obtain satisfactorily reproducible results has been by starting with a clean electrode at each c.d. and polarising at that c.d. until a steady value is reached. This method is very laborious and time-consuming, but it does lead to consistent and reliable results. The more frequently adopted method of measuring the potentials at a series of c.d.'s, without paying any specific attention to the time of polaristion factor, is in our view completely unreliable since the surface of the electrode is changing continuously throughout the observations and any overvoltages so determined are characteristic neither of a virgin anode nor of a fully polarised anode, nor can the values at different c.d.'s be fairly compared with one another.

Haissinsky has described a number of experiments the results of which are not in agreement with the hydrogen peroxide theory of electrolytic oxidation, and I freely admit the force of his observations. At the same time, the theory has provided a remarkably detailed explanation of a wide range of electrolytic oxidations. It is best regarded, I think, as an approximation to the truth which has considerable practical value in its own field but which will require substantial modification before it can embrace all anodic phenomena.

V. ANODIC PROCESSES AND CELL REACTIONS IN GENERAL

OXIDATION BY ANODIC PROCESSES AND BY HYDROGEN PEROXIDE

By M. Haïssinsky.

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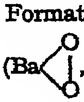
When hydrogen peroxide acts as an oxidising agent on an inorganic compound dissolved in water, the reaction may be one of the following types:

(*a*) Change of valency ($Co^{II} \rightarrow Co^{III}$, $Mn^{II} \rightarrow Mn^{IV}$, $Tl^{I} \rightarrow Tl^{III}$);

(*b*) Formation of an —O—O— bond without change of valency (, pertitanates, permolybdates);

(*c*) Formation of an addition compound by dipole-dipole action ($Cd(OH)_2 . xH_2O_2$; $La(OH)_3 . xH_2O_2$; probably $NaBO_2 . H_2O_2$).

We shall call "per-compounds" or "oxygen-bridge compounds" the compounds formed in the last two cases where there is no change of valency. On the basis of known experimental data,[1] the oxidising action of H_2O_2 on the inorganic compounds of all the chemical elements has been compared with that produced by electrolysis and, as a result, the following rules appear to hold.

(1) For an element having several valencies, the formation by H_2O_2 of an oxygen-bridge compound does not take place until after the transition of the element to his highest valency. Only one exception to this rule is known, viz., nitrogen for which the existence of a pernitrous acid has been reported.

(2) No metal is known which forms oxygen-bridge compounds by anodic oxidation;[2] only four metalloids, B, C, P, S, form such compounds by electrolysis.

(3) The elements whose electronegativities in Pauling's scale[3] as completed by the author[4] are smaller than or, at most, equal to 2·1, form per-compounds. Those whose electronegativities are greater than 2·1 generally do not form them. There are four exceptions to this rule; these are C, S, N, Hg, whose electronegativities are greater than 2·1 but which nevertheless give peracids or a peroxide containing an oxygen bridge.

The acids and the oxides of the elements having high electronegativities (corresponding to a high electrochemical potential), viz., $HBrO_3$, HIO_4 $HMnO_4$, Ni_2O_3, Au_2O_3, are generally reduced by H_2O_2.

(4) The higher insoluble oxides which are formed by anodic deposition all belong to elements having at least two valencies of which the lower one is the most stable.[5] In some cases the chemical composition of these compounds has not been completely elucidated, but it is always compatible with the valency of the element in the periodic system (except for the well-known cases Cu, Ag, Au).

Some of these higher oxides may be prepared as well by H_2O_2 but in basic solution only. It therefore seemed interesting to examine the effect of the addition of H_2O_2 upon their electrolytic formation. Together with Cottin[6] we prepared anodic deposits on Pt, the higher oxides of the following metals: (1) Ni, in a boric acid buffer solution at pH, 9·7; (2) Co, in acetic acid solution, pH, 6·9; (3) Mn, in acetic acid solution, pH, 5·2; (4) Ag, in acetic acid solution, pH, 4·5; (5) Po, in N. NaOH; (6) Pb, in N. HNO_3.

In all these cases the addition of a few drops of H_2O_2 stops the deposition and rapidly dissolves the deposit already formed.[7] The result is easily explained by the mutual reduction of hydrogen peroxide and the higher oxides under the conditions reported. It shows nevertheless that H_2O_2 is exercising an inhibiting action upon the anodic formation of the higher oxides and that consequently its existence at the anode is improbable under the normal conditions of their formation.

[1] *J. Chim. Physique*, 1947, **44**, 181.

[2] This rule applies strictly only to anodes of Pt, because only a few researches appear to have been done with other anodes.

[3] *The Nature of the Chemical Bond* (New York, 1945), p. 64.

[4] *J. Physique*, 1946, **7**, 7. The electronegativities have been calculated here from the heats of formation of oxides. This rule is accounted for by the fact that the electronegativity of hydrogen is 2·1 (see Haïssinsky, *J. Chem. Physics*, 1947, **15**, 152.

[5] The author has observed the anodic formation of protoactinium peroxide for quantities of the order of 10^{-8} g. of Pa in solution. The nature of this peroxide, originally attributed to the oxygen-bridge type of bond, cannot be established with certainty until its formation is verified on larger quantities and until the question of the valences of Pa is further elucidated.

[6] *Compt. rend.*, 1947, **224**, 392, 467.

[7] The prevention of the anodic deposition of Po in acid solution by H_2O_2 has already been observed by Joliot (*J. Chim. Physique*, 1930, **27**, 119). The same effect on the anodic deposition of Bi was noted in nitric acid solution and in basis tartaric solution (Haïssinsky and Sanielevici, *ibid.*, 1939, **36**, 54).

Of greater significance are the experiments performed by us on the anodic production of potassium percarbonate and sodium perborate. The electrolysis was carried out under the usual conditions of preparation of these substances, viz., low temperature, high c.d., and use of a porous diaphragm; the anode was of Pt, Pb, or graphite. Two identical saturated solutions of K_2CO_3 was submitted to electrolysis, but to one, three drops of H_2O_2 were added. The concentration of H_2O_2 + percarbonate during electrolysis was determined colorimetrically by addition of $Ti(SO_4)_2$ to drops of each solution, thereby forming the orange pertitanic acid. The results are shown in Fig. 1.

Similar curves have been obtained for sodium perborate using a Pt anode. With a graphite anode the two processes, formation of persalt and decomposition of H_2O_2, are slower so that the curve corresponding to the solution initially containing H_2O_2 crosses the other one after 100 min., and then continues slightly below the curve for the solution without H_2O_2.

Without delving into the kinetic details of the processes one can see that the decomposition of H_2O_2 predominates over the formation of the

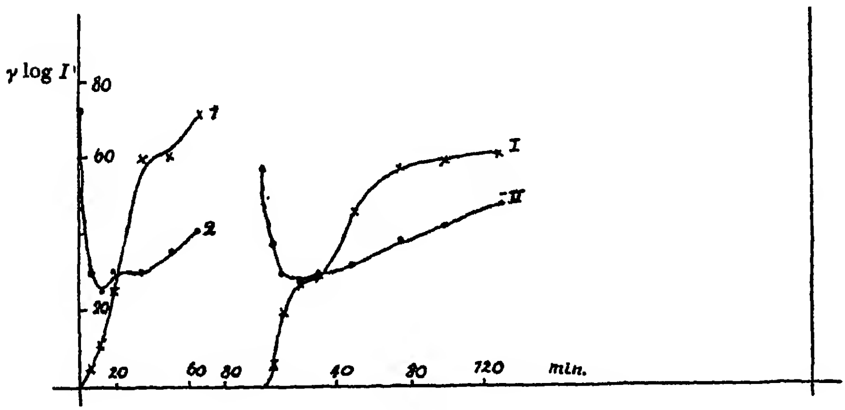


FIG. 1.

Pt anode $\begin{cases}\text{without } H_2O_2\text{—1,}\\ \text{with } H_2O_2\text{—2.}\end{cases}$ Pb anode $\begin{cases}\text{without } H_2O_2\text{—I,}\\ \text{with } H_2O_2\text{—II.}\end{cases}$

per-compounds and that here too, the reagent, far from favouring the oxidation, acts as an inhibitor.

Glasstone and Hickling,[8] the originators of the theory of the intermediate formation of hydrogen peroxide at the anode, suggested that this mechanism should be applied, amongst others, to the electrolytic production of percarbonates and perborates. Our experiments appear to exclude the possibility of such a mechanism.

It is known on the other hand, that the percarbonate formed by electrolysis is $K_2C_2O_6$, while the one formed by H_2O_2 is K_2CO_4, which is considered by Foerster[9] as an addition compound $K_2CO_3 . H_2O_2$. In the same way, Caro's acid which is formed by the action of H_2O_2 on SO_3 is the addition compound $SO_3 . H_2O_2$ and its salts are unknown,[10] whereas dipersulphuric acid $H_2S_2O_8$ is the product of electrolysis.

It is also useful to note that the four persalts which can be obtained by electrolysis are the only ones for which a mechanism of formation by means

[8] *Electrolytic Oxidation and Reduction* (London, 1935); *Chem. Rev.*, 1939, 25, 407.
[9] *Elektrochem. Wässer. Lösungen* (Leipzig, 1923), p. 853.
[10] Wells, *Structural Inorg. Chem.* (Oxford, 1945), p. 302.

of a direct discharge of anions can be postulated:

$$2\,SO_4^{--} = S_2O_8^{--} + 2e, \text{ or } 2\,SO_4H^- = S_2O_8^{--} + 2\,H^+ + 2e,$$
$$2\,PO_4^{---} = P_2O_8^{--} + 4e\,;\ 2\,CO_3^{--} = C_2O_6^{--} + 2e\,;\ BO_3^{---} = BO_3^- + 2e.$$[11]

Such a simple mechanism is impossible for other persalts, which are produced by H_2O_2 and not by electrolysis.

$$TiO_3^{--} \rightarrow TiO_4^{--}\,;\ VO_3^- \rightarrow VO_4^{--}\,;\ TaO_3^- \rightarrow TaO_4^-\,;$$
$$MoO_4^{--} \rightarrow MoO_5^{--}\,;\ UO_2^{++} \rightarrow UO_5^{--}, \text{ etc.}$$

The difficulty of the production of H_2O_2 and its derivatives at the anode can most probably be accounted for by the same explanation used to account for the inhibiting action on the anodic oxidations reported above, i.e., by the mutual reduction of these two classes of compounds. Bowden,[12] Hoar [13] and especially Butler and Drever [14] have shown that an anode of a noble metal such as Pt, Rh, Au, etc., *before reaching the overvoltage necessary for the oxygen evolution*, is covered at first with a monomolecular layer of oxygen and later with greater or lesser amounts of a "peroxidic" deposit, or more correctly with a deposit of a higher oxide. This is in agreement with older, more qualitative, observations.[15] Even if we assume then the possibility of a direct discharge, i.e., $OH^- = OH + e$, as postulated by Glasstone and Hickling, but as yet not proved, these radicals or the molecule H_2O_2 finally formed would immediately react with the active oxygen of the anodic deposit with mutual reduction:

$$Me\langle^{O}_{O} + 2\,OH = MeO + H_2O + O_2.$$

On the contrary, Glasstone and Hickling suppose that H_2O_2 exists at the anode in *a layer of high local concentration*, and that the difficulty of its detection is due to its catalysic decomposition by the metal surface. But it has been known since the work of Traube (1882) that H_2O_2 can be formed at the *cathode* by oxygen reduction. It has been shown [16] that $Ti(SO_4)_2$ may be transformed quantitatively into pertitanic acid, in the presence of oxygen, at a cathode of Ag or Au amalgam and more slowly at a cathode of smooth Pt, but the preparation of this peracid at the anode has as yet been unsuccessful.[17] Thus, in spite of the catalytic decomposition on the metal, H_2O_2 and its derivatives can be formed at the cathode but not at the anode.

This conclusion is confirmed by experiments on the corrosion of Al of Churchill,[18] who observed the formation of small amounts of H_2O_2 which increased in quantity with c.d. when the metal acted as cathode and which diminished sharply and disappeared when it acted as anode.

Perhaps the most serious objection against the theory of Glasstone and Hickling is that, without direct proof, it tends to reduce to a single mechanism a great number of anodic processes which take place under very different conditions. Without excluding completely the possibility of the formation of H_2O_2 under some particular conditions and on some particular anodes (e.g., carbon anodes), this phenomenon is certainly too

[11] The perborate is formed more probably through the intermediate formation of percarbonate, since the presence of carbonate is necessary to catalyse this anodic reaction (Engelhardt, *Tech. Elektrochem.*, (Leipzig, 1933), p. 158.

[12] *Proc. Roy. Soc. A.*, 1929, **125**, 446.

[13] *Ibid.*, 1933, **142**, 628.

[14] *Trans. Faraday Soc.*, 1936, **32**, 427.

[15] See, for instance, Marie, *Compt. rend.*, 1908, **146**, 477; Wöhler, *Z. Elektrochem.*, 1909, **15**, 769; *ibid.*, 1910, **16**.

[16] Haïssinsky and Emmanuel, *J. Chim. Physique*, 1937, **34**, 641.

[17] Attempts at the anodic preparation of Th and U peroxides gave also no results. Furthermore, Bancroft and Murphy (*J. Physic. Chem.*, 1939, **35**, 377), did not observe the anodic formation of perchromic acid.

[18] *Trans. Electrochem. Soc.*, 1939, **76**, 77.

rare and the anodic processes are too complex to have the general character supposed by them.

These authors are probably correct in criticising Walker and Weiss [19] who explain the action of all the catalysts in anodic oxidations by overvoltage, but it is no more obvious that this action may be interpreted by another single mechanism.[20] Some catalysts might, for instance, favour the decomposition of the polythionates (in the reaction $S_2O_3^{--} \rightarrow S_4O_6^{--}$ studied by Glasstone and Hickling) which contains a —S—S— bridge in a way similar to that in which they act upon the —O—O bond of H_2O_2 and its derivatives. In other cases the mechanism of the formation of the anodic compound can be modified by the presence of the catalyst or by variation of the composition of the medium or by the nature and state of the electrode.

With Quesney [21] an investigation on the conditions of the formation of Ni peroxide at anodes of different materials was conducted. In particular, the critical potential of the deposit formation on Pt and PbO_2 as a function of the *p*H of the solution containing $Ni(OH_2)$ was measured and found to change linearly with the *p*H according to the relation :

$$E = E_0 + \frac{RT}{F} \ln (OH)$$

while upon Ni this change is represented by the equation :

$$E = E_0 + \frac{RT}{2F} \ln (OH)^3.$$

The latter relation is equally valid for the change of the equilibrium potential of the peroxide with the solution (with a small constant difference in the E_0 value). Notwithstanding the fact that the thermodynamic significance of this equation is not yet clear, it is obvious that the mechanism of the formation upon Ni is not the same as on other electrodes.

According to indications given by potential measurements on different anodes,[22] the higher oxide of polonium, PoO_3, is formed in basic solution by direct discharge of PoO_3^{--} ions, but in acid solution by a secondary reaction, probably involving nascent oxygen. Conversely, the transformation of sulphites into dithionates takes place, according to Butler and Leslie,[23] in acid solution by direct discharge and possibly in a basic medium through the agency of nascent oxygen.

In conclusion, attractive as it may seem, it is hardly possible to admit a general mechanism for different anode processes. The experimental facts show the necessity of looking for the most suitable mechanism in each particular case.

Résumé.

Les données expérimentales sur la formation de per-composés à pont d'oxygène —O—O— ou d'oxydes supérieurs avec changement de valence permettent d'établir certaines règles sur la tendance des éléments chimiques à subir des oxydations de ces types sous l'action de H_2O_2 ou par électrolyse. L'eau oxygénée agit comme inhibiteur dans la formation anodique des

[19] *Trans. Faraday Soc.*, 1935, 31, 1011.

[20] Bancroft has already shown (*Trans. Electrochem. Soc.*, 1937, 71, 53), with the example of the Mn salts, that the parallelism between the action of the catalysts on the decomposition of H_2O_2 and on the anodic oxidations, postulated by Glasstone and Hickling, is not always observed. To this example we have to add that of Cu salts, which do not catalyse the decomposition of H_2O_2 in acid solution and yet have a strong effect upon the anodic reactions studied by these authors.

[21] *Comp. rend.* 1946, 223, 792, and unpublished results.

[22] Haïssinsky, *J. Chim. Physique*, 1933, 30, 27.

[23] *Trans. Faraday Soc.*, 1936, 32, 435.

per-composés et des oxyges supérieurs. On conclut que la présence de H_2O_2 à l'anode et son rôle comme stade intermédiaire dans les processus anodiques sont peu probables.

Zusammenfassung.

Die experimentellen Angaben über die Bildung von Per-Verbindungen mit O—O Brücken oder von höheren Oxyden mit veränderter Wertigkeit gestatten die Formulierung gewisser allgemeiner Regeln bezüglich der Neigung der chemischen Elemente, sich Oxydationen dieser Art, entweder unter dem Einfluss von H_2O_2 oder auf elektrolytischem Wege, zu unterziehen. Wasserstoffperoxyd hat einen verzögernden Effekt auf die anodische Bildung von Per-Verbindungen und von höheren Oxyden, woraus gefolgert wird, dass es unwahrscheinlich ist, dass es an der Anode aufscheint und ein Zwischenprodukt in anodischen Prozessen ist.

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KINETICS OF ELECTRODE PROCESSES ON THE IRON ELECTRODE

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The behaviour of the iron electrode in alkaline solutions is characterised by the complexity of the electrode processes due to the diversity of compounds which iron forms with oxygen. The interest of investigators was early attracted by this problem. Faraday was the first to state that the presence of oxygen on the surface of iron hinders its dissolution in acids and this has been repeatedly confirmed in later investigations. In the case of the anodic dissolution of platinum in acids Ershler [1] succeeded in determining the least amount of oxygen necessary to retard appreciably the kinetics of the reaction. It is considerably less than that needed to form a monolayer.

In the experiments reported in the present paper we determined the amount of oxygen needed to passivate an iron electrode under various conditions and showed that it, too, may be very small.

I. Influence of an Oxide Film on the Anodic Passivation of Iron in Alkaline Solutions.

The process of anodic oxidation and cathodic reduction of iron in alkaline solutions was studied by Förster and others [2] especially in connection with the problem of the nickel-iron cell. In his experiments with powdered iron electrodes, Förster established that iron which has been preliminarily subjected to cathodic reduction forms $Fe(OH)_2$ upon anodic polarisation. This process comes to an end due to passivation of the iron after a certain amount of electricity has passed through the electrode. The mechanism of such anodic passivation of iron in alkaline solutions has been but sparingly studied so far.

It was shown by a number of investigators that the oxide film formed when iron is exposed to gaseous oxygen passivates the surface of the

[1] Ershler, *Acta Physicochim.*, 1944, 19, 139.
[2] Förster, *Z. Elektrochem.*, 1910, 16, 461; Faust, *ibid.*, 1907, 13, 161; Krassa, *ibid.*, 1909, 15, 490; Grube and Gmelin, *ibid.*, 1920, 26, 459.

iron e ectrode.[3] However, the least amount of oxygen necessary for passivation was not determined. We undertook some experiments to clear up this point. The method used in these experiments has been described in details elsewhere.[4, 5]

The experiments were carried out with smooth iron electrodes made of Hilger spectroscopically-pure iron rods or wire from the same material. The true surface of the electrode was 2-3·5 times greater than the apparent surface depending on the previous treatment and was determined from the amount of oxygen taken up by activated adsorption.[4] On smooth iron at room temperature, polarisation curves similar to Förster's had not been obtained so far due to the fact that even after cathodic polarisation the electrode surface did not become active. In order to obtain a smooth electrode in the active state it is necessary to remove oxygen from the electrode surface; this was accomplished by heating the iron in hydrogen at 600° C. and then transferring it to a solution saturated with hydrogen without exposure to air.[5]

The anodic polarisation curves obtained after this treatment have two arrests corresponding to processes which take place at constant potentials. The potentials in this paper if the contrary is not stated, are referred to the hydrogen potential in the same solution. The electrode does not change outwardly during the first arrest but then gradually turns brown after the second begins. The first arrest corresponds to the process, $Fe \rightarrow Fe(OH)_2$, the second, which is half as long, to the oxidation of $Fe(OH)_2$ to ferric hydroxide, which contains probably less water than $Fe(OH)_3$. Upon cathodic polarisation there appears an arrest equal in length to the second anodic arrest and corresponding to reduction of the ferric hydroxide to $Fe(OH)_2$. These conclusions respecting the stoichiometry of processes on the iron electrode are based on polarisation measurements and on the values of the potentials determined on interruption of the current; they differ somewhat from Förster's views.[2]

The yield of the first electrochemical process on the iron electrode * depends, as shown by our experiments, on a number of factors, in particular on the state of the surface. If the electrode surface is oxygen-free the yield on it is great. For example, in 2N. NaOH at a c.d. of 1×10^{-5} amp./cm.[2] it is equal to 8×10^{-2} coulomb/cm.[2] of true surface. After brief exposure to the air the electrode in the same solution is completely passive, i.e. the polarisation curve shows no arrests. The amount of oxygen adsorbed on the iron upon brief exposure to the air is, however, equivalent to only $2 \cdot 5 \times 10^{-3}$ coulomb/cm.[2]. The yield increases with the concentration of the alkali.

In a recent paper [4] we have reported data on the influence of definite amounts of adsorbed oxygen on the passivation of the iron electrode. Prior to this, the kinetics of oxygen adsorption on iron at temperatures ranging from 90° K. to 500° K. were investigated and it was shown that a definite amount of oxygen, depending on the temperature, is adsorbed rapidly, whereafter a second slow stage of adsorption follows. These results agree in part with those found by other authors.[6]

The apparatus used in these experiments allowed of combining the

[3] Freundlich, Patcheke and Zocher, *Z. physik. Chem.*, *A*, 1927, **128**, 321; 1927, **130**, 289; Evans, *Trans. Faraday Soc.*, 1923, **18**, 1; Tamann, *Z. anorg. Chem.*, 1919, **107**, 104; Kistiakovsky, *J. Physic. Chem. Soc.* (*Russ.*), 1925, **57**, 97

[4] Burstein, Shumilova and Golbert, *Acta Physicochim.*, 1946, **21**, 785.

[5] Kabanov and Leikis, *ibid.*, 1946, **21**, 769.

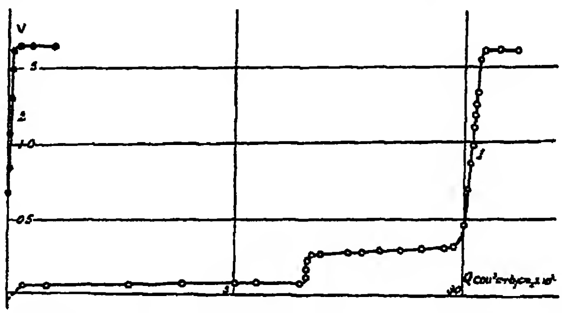
[6] Langmuir, *J. Amer. Chem. Soc.*, 1918, **39**, 1380; Gulbranson, *Trans. Electrochem. Soc.*, 1942, **81**, 327; 1942, **82**, 375; 1943, **83**, 301; Kochetkov, *Bull.* (*Isvestja*) *Acad. Sci. U.R.S.S.*, 1944, 320.

* The measure of the activity of iron, i.e. of its capacity to pass from the metallic state to $Fe(OH)_2$ upon anodic polarisation, is the quantity of electricity consumed in the process up to the passivation of the metal. This quantity will be called hereafter, " yield " of the electrochemical process.

gas adsorption technique with that used in electrochemical investigations. An iron wire 2·5 m. long and 0·2 mm. in diameter was reduced in hydrogen at 600° c. and outgassed at 850° at 1×10^{-6} mm. Hg; it was then allowed to adsorb oxygen and after being brought into contact with the outgassed solution was polarised anodically. The anodic polarisation curve of the outgassed, oxygen-free electrode is shown in Fig. 1 (curve 1).

These experiments showed that when oxygen is adsorbed to the amount of 2×10^{15} molecules per cm.^{2} of true surface * i.e. to an amount corresponding to the stage of rapid adsorption at room temperature, the

FIG. 1.—Dependence of the potential of an iron electrode on the quantity of electricity transmitted upon anodic polarisation (20°). Electrolyte 1·2 N. KOH. c.d. $1 \cdot 3 \times 10^{-5}$ amp./cm.^{2}. (1) Outgassed iron; (2) After adsorption of 4×10^{15} molecules of oxygen per cm.^{2}.



iron electrode retains its electrochemical activity at 20° c. In this case, too, the anodic polarisation curve obtained has two arrests. Entirely different is the behaviour of an iron electrode after adsorption of 4×10^{15} oxygen molecules per cm.^{2} of true surface (Fig. 1, curve 2). In this case the electrode becomes completely passive at 20° c., i.e. the anodic polarisation curve had no characteristic arrest. The amount of oxygen corresponding to the stage of rapid adsorption on iron at room temperature is thus not sufficient to passivate the electrode.

It appeared that the amount of oxygen necessary to effect passivation could be reduced by carrying out the polarisation at − 15° c.[7] These

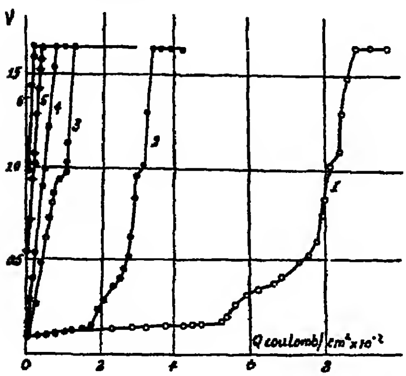


FIG. 2.—Dependence of the potential of an iron electrode on the quantity of electricity transmitted upon anodic polarisation (− 15° c.). Electrolyte 2·8 N. KOH. C.d. $1 \cdot 3 \times 10^{-5}$ amp./cm.^{2}.

(1) Outgassed iron;
(2) After adsorption of $0 \cdot 78 \times 10^{15}$
(3) ,, ,, $1 \cdot 5 \times 10^{15}$
(4) ,, ,, $1 \cdot 72 \times 10^{15}$
(5) ,, ,, $3 \cdot 5 \times 10^{15}$
(6) ,, ,, $7 \cdot 0 \times 10^{15}$
molecules of oxygen per cm.^{2}.

experiments showed that, in this case, upon the adsorption on iron of $0 \cdot 78 \times 10^{15}$ molecules of oxygen per cm.^{2} of true surface, the yield of the electrochemical process on the iron electrode is reduced by a factor of three. Upon adsorption of $1 \cdot 72 \times 10^{15}$ oxygen molecules per cm.^{2} of

* According to Emmett and Brunauer's data, the number of nitrogen molecules adsorbed per cm.^{2} of true surface necessary to form a monolayer is 6×10^{14}.

[7] Burstein and Shumilova (unpublished data).

true surface, i.e. of the amount corresponding to the rapid stage of adsorption at $-15°$ C., the iron electrode becomes passive (Fig. 2). With such an electrode the arrests on the charging curve corresponding to the formation of bivalent and trivalent iron compounds are no longer observed. Upon anodic polarisation at $-15°$ C. there appears an arrest at 0·95 V. corresponding probably to the formation of an oxide of a higher degree of oxidation. We shall return to this question further on. These data show that the normal electrochemical process in strong alkaline solution at $-15°$ C. ceases when the number of adsorbed oxygen molecules is approximately three times as large as Emmett and Brunauer's figure for the number of nitrogen molecules needed to form a monolayer. It is known from electronographic investigations [8] that when oxygen is adsorbed on iron Fe_3O_4 or γ—Fe_2O_3 is formed; hence when $1{\cdot}72 \times 10^{15}$ oxygen molecules are adsorbed per cm.^{2} of true surface, the resultant oxide film, if it were homogeneous, should be ca. 5·3 A. thick. This value is less than that corresponding to a unit cell of γ—Fe_2O_3.

It should be observed that in order to shift in the anodic direction the potential of an iron electrode rendered passive through deposition of oxygen, a comparatively large amount of electricity must be still expended. Experiments have shown in this case that the sum of the amount of oxygen deposited from the gas phase and the amount of oxygen which must be deposited in the process of anodic polarisation in a KOH solution to bring the potential up to e.g. 0·9 V., is approximately constant and equal to about 7×10^{15} molecules per cm.^{2} of true surface, which corresponds to $4{\cdot}3 \times 10^{-3}$ coulombs (Fig. 3).

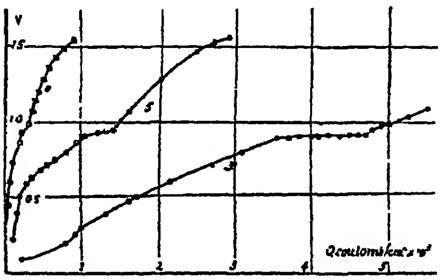


FIG. 3.—Curves 3, 5 and 6 of Fig. 2 on a different scale.

There is an essential difference between the course of the anodic polarisation of iron in dilute and in concentrated alkaline solutions.[9] If an electrode pre-heated in hydrogen is polarised anodically in a dilute solution of NaOH with sufficiently high c.d. then the iron behaves as if it were completely passive. In this case very small amounts of electricity are necessary to shift the potential of the iron electrode to the anodic side. For example, if $2\text{-}3 \times 10^{-4}$ coulomb is sent through 1 cm.^{2} of true surface in 0·05 N. NaOH at a c.d. of 1×10^{-5} amp./cm.^{2} the electrode potential is brought up to 0·2 V. After this treatment the electrode remains passive even if a more concentrated solution is substituted for the dilute one without exposing the electrode to the air.

The amount of electricity which passivates iron in dilute alkaline solution is therefore smaller than what is needed for the formation of an oxygen monolayer on the iron surface viz. *ca.* 4×10^{-4} coulomb/cm.^{2}.

A comparison of these data with the experiments on polarisation subsequent to the adsorption of oxygen from the gas phase leads to the conclusion that when oxygen is deposited from the gas phase the resulting film has a comparatively large number of vacant sites. This may perhaps be due to the bivalency of the oxygen molecules, which, as Langmuir has shown, makes it difficult to obtain a continuous layer. The vacant sites can interact with the ions of the solution.

[8] Nelson, *J. Chem. Physics*, 1937, **5**, 252; Winkel and Haul, *Z. Elektrochem.*, 1938, **44**, 611; Dankov and Shishakov, *Bull. (Isvestja) Acad. Sci. U.R.S.S.*, 1938, 1225.

[9] Kabanov and Leikis, *Acta Physicochim.* (in press).

2. The Mechanism of the Dissolution and Passivation of Iron in Alkaline Solution.

It has been shown in a number of experiments [9] that the yield of the electrochemical process $Fe \rightarrow Fe(OH)_2$ on an active electrode increases with increasing concentration of the alkali (Fig. 4) and decreasing c.d. The overvoltage of this electrochemical process is, however, almost independent of the concentration of the alkali and of the concentration of foreign anions (SO_4^{--}) and increases linearly with log c.d. The slope of the logarithmic curves at c.d.'s exceeding 10^{-6} amp./cm.^{2} equals 0·04 v., while at lower c.d.'s it is 0·02 v.

The capacity of the iron electrode as determined from the slope of the charging curves in dilute solutions or from the decay curves of the electrode potential when the polarising current is interrupted in the region of the first arrest in more concentrated solutions, is approximately 1500 μF/cm.^{2} of apparent surface.

On the basis of the experimental data reported above it is possible to advance a conception of the mechanism of the formation of $Fe(OH)_2$

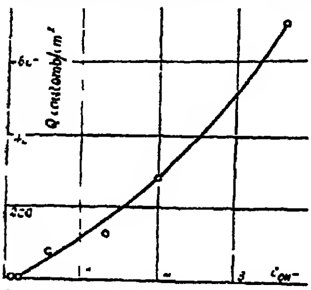


FIG. 4.—Dependence of the yield of the electrochemical process $Fe \rightarrow Fe(OH)_2$ on the concentration of the alkaline solution. The yield is given in coulomb/cm.^{2} of apparent surface.

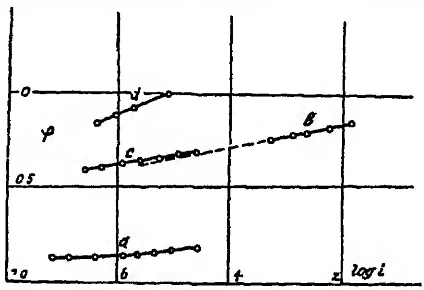


FIG. 5.—Potential of the anodic dissolution of iron against log c.d. The potential is here referred to the standard hydrogen electrode.

(*a*) 2N. NaOH; (*b*) N. HCl; (*c*) 0·05 N. NaOH + 2N. NaCl; (*d*) 0·5 N. NaOH + 2N. NaCl.

and the passivation of iron in alkaline solutions. To this end it will be useful to compare the data on the anodic dissolution of iron in alkali with the data on the anodic dissolution of iron in acids.[10] The comparison was made by extrapolating the overvoltage curve of the anodic process $Fe \rightarrow Fe^{++}$ in acid solutions to the potentials of the anodic process $Fe \rightarrow Fe(OH)_2$ in the case of active iron electrode in an alkaline solution (Fig. 5). The comparison shows that at equal potentials the anodic dissolution of iron in alkaline solutions proceeds *ca.* 10^4 times as fast as in acids. On the other hand in alkaline solutions the anodic process on iron slows down greatly with time and is finally completely stopped due to passivation, a circumstance which does not occur in acid solutions. This indicates that the mechanism of the dissolution of iron is widely different in acids and in alkalies.

Both the greater rate of dissolution and the passivation observed in alkalies are evidently due to anodic deposition of oxygen on the iron surface which is stimulated in alkaline solutions by the large concentration of hydroxyl ions. Thus in alkaline solutions the oxygen on the iron surface plays a double role—on the one hand accelerating dissolution, on the other hand passivating the iron and bringing finally the dissolution to an end. These general considerations may be developed in somewhat greater detail.

Upon anodic polarisation of iron, $Fe(OH)_2$ is deposited in the form of

[10] Kusnezov, *J. Russ. Physic. Chem.*, 1947, **21**, 201.

a gelatinous porous precipitate weakly bound to the metal. This has been concluded from the failure to detect any ohmic resistance on an electrode covered with a deposit of $Fe(OH)_2$ although this compound is itself nonconducting. The structure of the ferrous hydroxide precipitate and its weak adhesion to the metal lead to the conclusion that it is deposited from a supersaturated solution and not formed directly from the metal. As was pointed out above, the reaction $Fe \rightarrow Fe^{++}$ is a slow process, at equal potentials, compared with the reaction $Fe \rightarrow Fe(OH)_2$; hence it cannot be an intermediate stage in the anodic formation of $Fe(OH)_2$ in alkaline solutions. As is known,[11] in alkaline solutions iron exists mainly in the form of $HFeO_2^-$ ions. Bearing in mind moreover that acceleration of the dissolution of iron in alkalies is connected with the adsorption of oxygen on iron, it is natural to assume that the intermediate product during the process of dissolution is a $HFeO_2^-$ ion which is formed on interaction of a surface iron oxide with the alkali :

$$(FeO)_{ads.} + OH^- \rightleftarrows HFeO_2^-.$$

Experiments show, however, that the potential of anodic dissolution of iron is not the reversible potential of the system $Fe/HFeO_2^-, OH^-$. A calculation of the increase in the concentration of $HFeO_2^-$ at the electrode surface on passing the current, based on the equations of non-steady diffusion (even assuming that in the initial stage of polarisation all the $HFeO_2^-$ ions formed remain in solution and precipitation of $Fe(OH)_2$ does not occur) shows that the experimentally-observed shift of the potential at the beginning of anodic polarisation of the active iron is considerably greater than what should correspond to an equilibrium potential of $Fe/HFeO_2, OH^-$.

It follows, on the other hand, from our data, that the process $Fe \rightarrow HFeO_2^-$ cannot be regarded as an irreversible reaction proceeding in one elementary act: $Fe + 3OH^- \rightarrow HFeO_2^- + H_2O + 2\ominus$. In fact, by computations similar to those used by Frumkin[12] in treating the kinetics of hydrogen overvoltage it can easily be shown that the anodic overvoltage of iron should decrease in this case by 0·12 v. when the concentration of alkali increases tenfold. This, however, does not take place. It should be noted that in computing the potential of the anodic process on iron we did not take into account the variation of the ζ-potential, as the introduction of SO_4^{--} ions into the solution does not affect the overvoltage of iron in dilute solutions.

Our data on the capacity of the iron electrode indicate that, in a certain potential range, an electrochemically-active oxygen adsorption layer is formed on the iron surface. The electrochemical deposition of oxygen may be assumed to be the first rapid stage of dissolution of iron in alkali. Judging by the magnitude of the capacity the amount of this oxygen at the potential of the first arrest comprises a fraction of a monolayer. This adsorbed labile oxygen can transform either in a surface oxide soluble in the alkali, or in a more firmly bound (passivating) surface oxide which retards further dissolution of the iron. Each of these processes requires addition of oxygen through an electrochemical reaction.

These considerations can be put in a more definite form by means of the following scheme. The first stage, which leads to the formation of an electrochemically-active layer of adsorbed oxygen is the discharge of OH^-

$$Fe + OH^- \rightleftarrows (FeOH)_{ads.} + \ominus \quad . \quad . \quad . \quad (1)$$

This is followed by the slow discharge of a second OH^- on the electrochemically-active surface oxide :

$$(FeOH)_{ads.} + OH^- \rightarrow (FeO)_{ads.} + H_2O + \ominus \quad . \quad . \quad (2)$$

The resulting surface ferrous oxide dissolves in alkali according to the equation

$$(FeO)_{ads.} + OH^- \rightleftarrows HFeO_2^- \quad . \quad . \quad . \quad (3)$$

[11] Schrager, *Chem. News*, 1929, **138**, 354.
[12] Frumkin, *Z. physik. Chem A*, 1933, **164**, 121.

On hydrolysis of the $HFeO_2^-$ ion a deposit of ferrous oxide if formed :

$$HFeO_2^- + H_2O \rightarrow Fe(OH)_2 + OH^- \quad . \quad . \quad . \quad (4)$$

It is easily seen that the rate of dissolution of iron upon anodic polarisation computed on the basis of this scheme (eqn. (2) and (1)) equals

$$i_A = K_1[FeOH]_{ads.}\,[OH^-]\,e^{\frac{\phi F}{2RT}} = K_2[OH^-]^2\,e^{\frac{3\phi F}{2RT}} \quad . \quad . \quad (5)$$

Let us denote by ϕ_r the reversible potential of the $Fe/Fe(OH)_2$, OH′ electrode. The overvoltage of the reaction η equals

$$\eta = \phi - \phi_r = \frac{2RT}{3F}\ln i - \frac{RT}{3F}\ln[OH^-] + const.$$

In a first approximation this agrees with our experimental data.

A similar mechanism of anodic dissolution of a metal was suggested earlier by Ershler.[1] He showed that in the presence of Cl^- ions the dissolution of platinum proceeds, not by direct transition of hydrated metal ions into the solution, but by way of formation of an intermediate surface platinum chlorine complex. In our case the hydroxyl plays the part of the chlorine.

Let us now consider the transformation of the electrochemically-active oxide into the passivating surface compound. As was observed above, iron is passivated when very small quantities of passivating oxides are formed on the surface. Inasmuch as a considerable amount of iron is dissolved in the time necessary for passivation, the active surface oxide obviously goes over into the soluble form many times faster than into the passivating one. At the same time the passivation process is more accelerated with increasing potential than the process of dissolution, as appears from the decrease of the yield of the process $Fe \rightarrow Fe(OH)_2$ with increasing c.d. Such a relation can exist if, e.g., the passivating oxide is formed as a result of the discharge of OH^- accompanied by the transfer of two electrons :

$$(FeOH)_{ads.} + OH^- \xrightarrow[\text{discharge}]{\text{slow}} \underset{\text{passivating oxide}}{(FeO,\,OH)_{ads.}} + H^+ + 2\ominus.$$

The rate of the process leading to the formation of the passivating oxide is then

$$i_p = K_3[FeOH]_{ads.}\,[OH^-]\,.\,e^{\frac{\phi F}{RT}} \quad . \quad . \quad . \quad (6)$$

The entire process of dissolution and passivation of iron in alkaline solutions can thus be represented by the following scheme :

$$\begin{tikzcd}
 & \underset{\text{dissolved}}{HFeO_2^-} \arrow[r, "+H_2O"] \arrow[d, shift left] & Fe(OH)_2 + OH^- \\
 & \underset{\text{soluble surface oxide}}{(FeO)_{ads.} + H_2O + \ominus} \arrow[u, shift left, "+OH^-"] & \\
Fe + OH^- \arrow[r, shift left] & \underset{\text{electrochem.-active surface oxide}}{(FeOH)_{ads.} + \ominus} \arrow[l, shift left] \arrow[u, "+OH^-", "\text{slow discharge}"'] \arrow[d, "+OH^-"', "\text{slow discharge}"] & \\
 & \underset{\text{passivating oxide.}}{(FeO,\,OH)_{ads.} + H^+ + 2\ominus} &
\end{tikzcd}$$

It cannot be claimed as yet that this scheme has been founded in all its details. We believe, however, that it renders satisfactorily the main features of the process.

We shall not consider here the kinetics of the passivation process in detail, observing merely that a considerable amount of iron is dissolved during passivation and hence the passivating oxide thereby formed must be partially removed from the surface. A complete theory should explain the progressive accumulation of passivating oxide despite its continuous removal, and take into account that the velocity of the reaction stages given by eqn. (1) and (2) decreases with increasing surface concentration of the passivating oxide. The process of accumulation of passivating oxides is probably to some extent analogous to the self-accelerating process of crystallisation. The yield of the reaction $Fe \rightarrow Fe(OH)_2$ at any rate should increase with the ratio of the initial rates of the active (eqn. (5)) and passivating (eqn. (6)) processes:

$$\theta = f\left(\frac{A}{i_p}\right) = f\left(\frac{[OH^-]^{\frac{1}{2}}}{i^{\frac{1}{2}}}\right) = f_1\left(\frac{[OH^-]}{i^{\frac{1}{2}}}\right) \quad . \quad . \quad . \quad (7)$$

where f_1 is, as yet an undetermined, increasing function of the argument, $[OH^-]/i^{\frac{1}{2}}$. According to eqn. (7) the yield should fall with increasing anodic c.d. and rise with increasing concentration of the alkali, which is actually observed.

The study of the dissolution and passivation of iron in alkaline solutions and of the reduction of $Fe(OH)_2$ is being continued.

3. The Electrochemical Process at Potentials ~0·95 v.

Upon polarisation of iron in alkaline solutions we observed in several cases an arrest of the potential at approximately 0·93-0·95 v. (with respect to the hydrogen electrode in the same solution). Small arrests near the indicated value of the potential are obtained when molecular oxygen is present in the alkaline solution during cathodic and anodic polarisation of iron electrodes. The length of these arrests corresponds to $10^{-5}-5\times10^{-3}$ coulomb which is equivalent to a quantity of oxygen ranging from a small fraction of a monolayer to a few monolayers.[13]

A similar arrest can be obtained when iron, after reduction in hydrogen and outgassing at high temperature, is anodically polarised in dilute KOH solution. In this case the length of the arrest may correspond to as much as 50×10^{-3} coulomb/cm.².[7]

A small arrest is also observed on an iron electrode partially covered with oxygen adsorbed from the gas phase ($1·5 \times 10^{15}$ molecules/cm.²), if the anodic polarisation is carried out at low temperature (−15°). With a larger adsorbed amount equal to 7×10^{15} molecules per unit area no arrest is observed. Hence adsorbed oxygen passivates this process too (Fig. 3).

If passive iron is treated with hydrogen peroxide which is then removed from the solution, a cathodic and an anodic arrest are also observed in the same region of potentials. The overvoltage of the process corresponding to these arrests is less than that of other processes on an iron electrode in alkaline solutions.[14] It has not been proved as yet that the arrests in all these cases correspond to the same process, nor is the question of the composition of the resultant oxide clear.

[13] Kabanov and Vanjukova (unpublished data).
[14] Kabanov and Derjaguina (unpublished data).

4. Anodic Oxidation of Iron in the Presence of Chlorine Ions.

If iron oxidised in air is anodically polarised in an alkaline solution containing sodium chloride (e.g. in 2 N. concentration), then at low concentration of the alkali the electrode potential does not rise to the potential of oxygen evolution, but reaches a maximum value and then gradually decreases. In order to explain the mechanism of this effect which was first described by Haber and Goldschmidt,[15] we investigated the processes taking place during this decrease and after a stationary potential was attained.[13]

The anodic process in this case, too, consists in metallic iron going over into $Fe(OH)_2$. However, in contradistinction to the similar process in pure alkaline solutions, in the presence of Cl^- ions it can continue indefinitely unaccompanied by passivation of the iron. The overvoltage of this process under certain conditions can reach high values, e.g. 1·4 V. and more; it increases linearly with log c.d., with a coefficient which varies from 0·04 to 0·12 V., depending on the composition of the solution. At constant c.d. the greater the concentration of Cl^- ions and the smaller the concentration of OH^- ions the lower will be the potential; the relation between the concentration of these ions and the potential is linear. However, as the ratio $[Cl^-]/[OH^-]$ is increased, the steady potential will decrease only down to a certain limit. This minimum value of the potential of anodic formation of $Fe(OH)_2$ in the presence of Cl^- ions coincides with the potential observed at the same c.d. in the case of the anodic dissolution of Fe in acids. The latter was found by extrapolating Kusnezov's [10] polarisation curve for the anodic dissolution of iron in HCl to the c.d.'s at which the iron electrode was polarised in alkaline solutions of chlorides (Fig. 5).

The difference between the dissolution of iron in alkaline solutions of chlorides and in pure alkalies and the similarity between the former process and the dissolution in acids leads us to believe that the first slow stage of the process $Fe \rightarrow Fe(OH)_2$ in alkaline solutions of chlorides is the ionization of iron $Fe \rightarrow Fe^{++}$. The second, fast stage, is the chemical reaction: $Fe^{++} + 2OH^- \rightarrow Fe(OH)_2$ with the possible intermediate formation of the cation $FeOH^+$.

The Cl^- ion allows Fe^{++} to be formed, but does not participate in the process itself. This is evident, for instance, from the fact that when the concentration of Cl^- ions in 0·01 N. NaOH solution is varied from 0·01 N. to 4 N. the rate of the process $Fe \rightarrow Fe(OH)_2$ remains unaffected and equal to the rate of the process $Fe \rightarrow Fe^{++}$ in acid at the same electrode potential. The accelerating effect of Cl^- ions on the corrosion of iron is thus due to the fact that it hinders the passivation of iron by adsorbed oxygen which otherwise would put an end to the dissolution of the iron.

As was observed above, the rate of the process takes off with increasing concentration of the alkali but not with time. This shows that a stationary concentration of the passivating agent establishes itself on the surface of the iron electrode, which increases with increasing concentration of the alkali. At sufficiently high concentrations of alkali and high c.d.'s the process $Fe \rightarrow Fe(OH)_2$ ceases completely, the iron becoming passive not gradually, as in pure alkali, but abruptly. A lowering of the c.d. reactivates the iron.

The following circumstance is essential for an understanding of the mechanism of this process. It was snown that in solutions containing Cl^- ions and OH^- ions in 2 N. concentration the charging curves of passive iron are twice as steep as in solutions devoid of chlorine ions. This means that the chlorine ions adsorbed on passive iron hinder the deposition of oxygen on the iron.

Ershler was the first to observe a decrease of the electrode capacity

[15] Haber and Goldschmidt, *Z. Elektrochem.*, 1906, **12**, 49; Britton and Evans, *J. Chem. Soc.*, 1930, 1780.

due to chlorine ions upon the polarisation of platinum in acid solutions (for references, see paper of Ershler in this issue). His explanation was that the adsorption of chlorine retards the deposition of oxygen on the platinum surface. In this case, however, the process is not a steady one, as oxygen is gradually accumulated on the surface and finally stops the dissolution of the metal. In the case of iron in the presence of Cl^- ions, if the concentration of OH^- ions is not too great, a steady process is observed.

It may be assumed that chlorine displaces the hydroxyl from the iron electrode surface and thus prevents the deposition of oxygen and consequently the formation of passivating oxides. This allows the process $Fe \rightarrow Fe^{++}$ to proceed indefinitely; on the other hand the adsorption of chlorine prevents the iron from being dissolved by way of intermediate oxygen adsorption.

An increase in the positive potential facilitates the displacement of adsorbed oxygen by chlorine ions. As a result of this, if an iron electrode becomes covered with very firmly adsorbed oxygen due to the action of air or to anodic polarisation, then upon anodic polarisation in the presence of chlorine the electrode potential first rises to a definite maximum and then gradually falls off to a steady value (Fig. 6). The anodic process in this case does not take place at first over the whole surface but only in microscopic pores of the oxide film; however, as the process continues

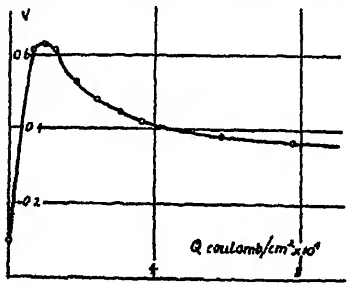


FIG. 6.—Dependence of the potential of iron previously passivated through contact with air on the quantity of electricity transmitted in

0·1 N. NaOH + 2N. KCl.

c.d. 10^{-4} amp. per cm.^{2}. Potential referred to hydrogen electrode in the same solution.

the oxide film previously formed gradually loses contact with the metal and disaggregates.

The above point of view is different from the interpretation given by Evans. It appears to us that the activating effect of anions like Cl^- is due to an adsorption effect, i.e. to the displacement of oxygen from the surface of iron, and not to a special ability for penetrating the oxide film.

The foregoing considerations on the mechanism of anodic dissolution of iron in the presence of Cl^- bear a preliminary character. Experimental facts like the linear increase of the overvoltage with concentration of the alkali and decrease with concentration of Cl^-, complete passivation upon increase in the c.d. and the accompanying periodic phenomena stand still in need of a more detailed study.

Summary.

It is shown that upon anodic polarisation in alkaline solutions at room temperature a smooth iron electrode from the surface of which oxygen was removed goes over into $Fe(OH)_2$ which is afterwards oxidised to trivalent iron. The electrochemical transition of iron to $Fe(OH)_2$ proceeds with a low overvoltage, but after some time the process ceases due to the formation of passivating surface oxides. The greater the concentration of OH^- ions the greater is the quantity of iron participating in the reaction. The iron does not go over into $Fe(OH)_2$ at room temperature if prior to anodic polarisation an amount of oxygen corresponding to $2{\cdot}5 \times 10^{-3}$ coulomb/cm^2 of true surface is deposited from the gas phase. If the anodic polarisation is carried out at $-15°$ c. the necessary quantity of

oxygen corresponded to $1 \cdot 1 \times 10^{-3}$ coulomb/cm.². Upon anodic polarisation in dilute alkali passivation sets in when the amount deposited is only 2×10^{-4} coulomb/cm.² of true surface.

A mechanism is proposed to explain the relation between the formation of $Fe(OH)_2$ and the passivation of iron upon anodic oxidation. The mechanism of the anodic dissolution of iron in the presence of both Cl^- and OH^- ions in the solution is also discussed.

Résumé.

Une électrode de fer lisse, dont la surface a été débarrassée d'oxygène, est transformée en $Fe(OH)_2$ (qui est ensuite oxydé en fer trivalent) par polarisation anodique en solution alcaline à température ordinaire. Le phénomène a lieu à un faible survoltage, puis cesse par suite de la formation d'oxydes, qui rendent la surface passive. Il peut être complètement empêché, si, avant la polarisation, de petites quantités d'oxygène sont déposées en phase gazeuse sur l'électrode. On propose deux mécanismes pour rendre compte de ces faits, ainsi que de la dissolution anodique du fer, lorsque les deux ions Cl et OH sont présents dans la solution.

Zusammenfassung.

Eine glatte Eisenelektrode, von deren Oberfläche aller Sauerstoff entfernt ist, wird bei anodischer Polarisation in alkalischer Lösung bei Zimmertemperatur in $Fe(OH)_2$ verwandelt (das darauf zu dreiwertigem Eisen oxydiert wird). Diese elektrochemische Reaktion verläuft bei geringer Überspannung, aber wird nach einiger Zeit durch die Bildung von passivierenden Oberflächenoxyden aufgehalten. Sie kann verhindert werden, wenn vor der Polarisation geringe Sauerstoffmengen aus der Gasphase an der Elektrode abgeschieden werden. Es wird ein Mechanismus zur Erklärung dieser Vorgange vorgeschlagen, sowie auch einer, der die anodische Auflösung des Eisens, wenn Cl′ und OH′ zusammen in der Lösung vorhanden sind, zu erklären vermag.

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INVESTIGATION OF ELECTRODE REACTIONS BY THE METHOD OF CHARGING-CURVES AND WITH THE AID OF ALTERNATING CURRENTS.

BY B. ERSHLER.

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I. The Kinetics of the Formation of Adsorbed Layers of Oxygen and Hydrogen on Metals.

The obtaining of charging-curves, i.e. of curves showing the dependence of the potential on the amount of electricity passed, affords a convenient method of investigating the kinetics of formation of hydrogen and oxygen layers on electrodes especially when varying c.d.'s are used.

In so far as the formation and removal of adsorbed layers proceed with a measurable velocity, these layers may be in equilibrium only when

charging the electrode sufficiently slowly, so that only in this case information concerning equilibrium properties may be obtained from charging-curves. When charging more rapidly the adsorption layers have no time to attain equilibrium, so that a direct determination of the velocity of formation and removal of adsorbed layers may be attained. Some results obtained on Pt, Ag and Au with slow and rapid charging are reported below.

(*a*) **Slow Charging.**—It was already pointed out [1] that on slow charging of platinum charging-curves are obtained which exhibit three distinct regions.[2, 3] In the neighbourhood of the hydrogen potential the slope of the curves is small, i.e. the potential rises slowly as the electrode is charged; at more anodic potentials the slope increases and at still more anodic potentials the curves become again less steep. A comparison of the amount of electricity needed to change the potential of the platinum in these three ranges with the corresponding changes in the charge of the double-layer, as determined by an independent method, offered proof [4] that in the region of the steep rise of the curves the polarising current is spent mainly, or at any rate to a considerable extent, on charging the double-layer. The lower arrest at cathodic potentials is interpreted as

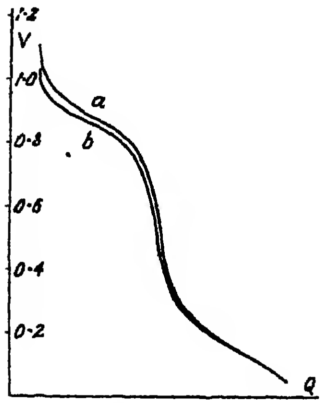


FIG. 1.—Charging-curves of platinised platinum in N. H_2SO_4.

(*a*) Cathodic polarisation immediately after oxidation in moist oxygen at room temperature during 24 hr.

(*b*) Cathodic polarisation after oxidation under similar conditions. After the oxidation the electrode was kept for 4 days in nitrogen.

Q Amount of electricity passed through the electrode.

due to the formation of a layer of adsorbed hydrogen, the upper one to oxidation of the platinum. Whereas in the neighbourhood of the hydrogen potential the slow charging-curves are reversible, which has permitted a number of conclusions to be drawn concerning the thermodynamical properties of the adsorbed hydrogen layer on platinum,[5, 6] at anodic potentials reversible curves cannot be obtained, even when charging extremely slowly. Hence, strictly speaking, the upper arrests of the curves at anodic potentials cannot be used to determine the thermodynamic properties of the surface oxides which form at these potentials. Nevertheless, as stated by A. Frumkin, investigations of oxide layers carried out in his laboratory using the method of slow charging have made it possible to draw certain general conclusions concerning the properties of these layers.

1. The strength of the bond between the metal and oxygen increases with time.

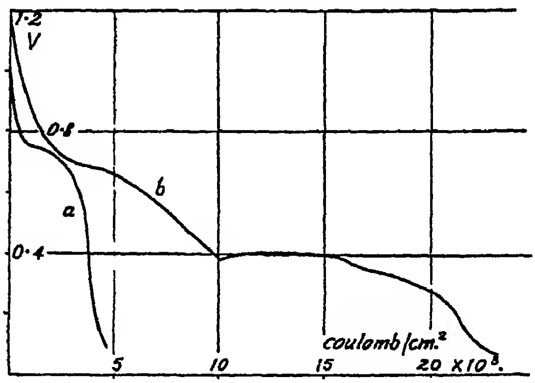
An increase of this kind is observed either when applying prolonged

[1] Ershler and Frumkin, *Trans. Faraday Soc.*, 1939, **35**, 464.
[2] Šlygin and Frumkin, *Compt. rend. U.R.S.S.*, 1934, **2**, 173; *Acta Physicochim.*, 1935, **3**, 791.
[3] Ershler, *ibid.*, 1937, **7**, 327.
[4] Frumkin, Šlygin and Medvedovsky, *ibid.*, 1936, **4**, 911.
[5] Frumkin and Šlygin, *ibid.*, 1936, **5**, 819.
[6] Temkin, *J. Russ. Physic. Chem.*, 1941, **15**, 296.

anodic polarisation at a given potential, or when allowing a sufficient lapse of time after oxidation by molecular oxygen.[7, 8]

In Fig. 1 are given cathodic charging-curves in N. H_2SO_4 of platinised platinum electrodes, subjected to a previous oxidation in moist oxygen for 24 hr. (according to Nesterova). Curve *a* was taken immediately after oxidation of the electrode, curve *b* after the oxidised electrode was kept for 4 days in an atmosphere of nitrogen. The arrest on the curves at about 0·9 v. corresponds to the removal of adsorbed oxygen and that below 0·3 v. to the formation of a hydrogen layer. During the time the electrode had been kept in nitrogen the bond between oxygen and the metal became stronger, which is expressed by the fact that the removal of oxygen proceeds at less positive potentials as seen from the curves in Fig. 1. The hydrogen arrests on curves *a* and *b* are identical. A strengthening of the same kind is observed when raising the oxidation temperature of the platinum.

When applying anodic polarisation to a smooth platinum electrode in N. H_2SO_4, as has been shown by Obrucheva, the increasing strength of the bond with growing anodic potential results in the formation of oxides



Volts.

FIG. 2.—Charging-curves of smooth platinum in N. H_2SO_4.

(*a*) Cathodic polarisation after anodic oxidation in N. H_2SO_4 by c.d. 10^{-3} amp./cm.².
(*b*) Cathodic polarisation after anodic oxidation by c.d. 10^{-1} amp./cm.².
Subsequently to the anodic oxidation the electrode was gently washed to remove the oxygen saturated solution from the surface.

possessing already phase properties. In Fig. 2 are shown cathodic charging-curves of a Pt-electrode, which had previously been subjected to anodic polarisation by c.d.'s of 10^{-3} and 10^{-1} amp./cm.². Although in the first case the amount of oxygen on the electrode surface already greatly exceeds that necessary to form a monolayer of oxide,* the oxide film does not show phase properties. On the second curves an arrest is observed at 0·4 v., which possesses all the characteristic properties of a phase transition. On cathodic reduction of the more stable oxides a slow removal of oxygen is observed, the velocity of which cannot be increased by shifting the potential towards more negative values, which points to a deeper penetration of oxygen into the metal lattice.

2. The oxidation processes affect the adsorption properties of the metal

[7] Obrucheva and Nesterova (unpublished data).
[8] Frumkin, *J. Physic. Chem.* (*Russ.*), 1940, 14, 1200.
* It is noteworthy, that on anodic oxidation of a platinum wire such comparatively thick oxide films are easily formed whereas in the case of platinised platinum at the same anodic potential the amount of oxygen deposited on the surface remains in the limits of a monolayer.[7]

surface. This can be shown by subjecting smooth platinum previously oxidised as described above to cathodic reduction and then obtaining an anodic charging-curve with low c.d. In this case the adsorption of oxygen is greatly facilitated and occurs at potentials at which the "normal" platinum surface is not yet oxidised.

The influence of the oxidation on the adsorption properties of metallic surfaces has been shown by Rakov [9] to be still more marked in the case of silver. Etched silver oxidised in air at room temperature, acquires in 0·1 N. KOH a potential which is by about 1 V. more positive than the reversible hydrogen potential; when applying to it a cathodic polarisation with low c.d.'s (of the order of 10^{-7} amp./cm.^{2}) curve 1, Fig. 3, was obtained, from which it is seen that the adsorbed oxide layer does not possess phase properties, for it is removed within a very wide potential range. A curve of the same shape is also obtained with smooth Ag. The anodic charging-curve of ordinary silver has a similar shape, i.e. in the case of electrochemical oxidation a non-phase oxide is also obtained. The picture is completely changed on oxidising silver at 800° C. As is well known, at this temperature bulk oxides of silver cannot form. Nevertheless, the cathodic polarisation curve of silver thus treated (curve 2, Fig. 3) shows that there is a very firmly adsorbed oxide layer on its surface, which

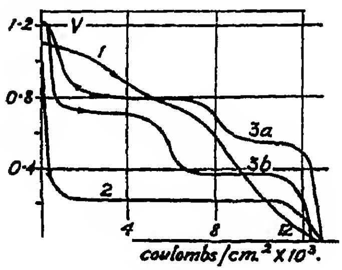


FIG. 3.—Charging-curves of Ag in 0·1 N. KOH (c.d. $5 \cdot 10^{-7}$ amp./cm.^{2}) for different preliminary treatments of a silver electrode.
1. Cathodic polarisation of ordinary Ag, oxidised in air at room temperature.
2. Cathodic polarisation of Ag oxidised at 800° C.
3*a*. Anodic polarisation of Ag after curve 2 has been taken.
3*b*. Cathodic polarisation of Ag after curve 3*a* has been taken.
As can be seen from the length of the arrests in curves 2, 3*a* and 3*b* the real surface of the metal is increased after it has been oxidised at 800° C.

possesses phase properties, in so far as it is reduced at an almost constant potential as seen from the horizontal arrest on the curve. After the removal of this layer by means of cathodic polarisation the silver surface substantially differs from that of ordinary untreated silver. This is seen from the anodic and cathodic charging-curves obtained on such silver (curves 3*a* and 3*b* respectively), on which two characteristic horizontal arrests appear. Apparently ordinary silver has a random surface structure characterised by the presence of sites with different energies of oxygen adsorption, whereas the surface of silver oxidised at 800° is much more uniform.

(*b*) **Rapid Charging.**—During rapid charging, formation and removal of the atomic layers at the corresponding potentials are not completed. Thus, the removal of adsorbed hydrogen from platinum on rapid anodic polarisation will not be completed at the potentials of the hydrogen range of the charging-curve; part of the hydrogen will be removed at potentials corresponding to the double-layer range. Such "blurring" of the hydrogen and oxygen arrests results in a smoothing-out of the charging-curve at higher c.d.'s, the separate regions of the curve occasionally merging into a straight line or shifting along the potential axis. This is facilitated by the presence of substances poisoning the electrode surface. The amounts of electricity delivered by the current on the various parts of such curves have no longer any simply physical meaning. Particularly the capacity in the double-layer region will always be too high as com-

[9] Rakov, *Thesis* (Moscow, 1947).

pared with equilibrium values since electricity in this case will be expended not only in charging the double-layer, but also in forming or removing atomic layers. When the electrode surface is kept clean and the charging is not too rapid (charging time 1/100 sec. for the entire curve) it is possible to obtain curves [10] which preserve, in the main, a correct form. Curves for platinum closely approaching equilibrium conditions are also given in Hickling's latest paper.[11] It should be observed that on the latter curves the capacities in the double-layer range are still too great—of the order of 300-400 $\mu F/cm.^2$, which is probably due to overlapping of the hydrogen arrest on the double-layer range as a result of rapid charging. The deviation of the charging-curves obtained, when the electrode is charged in such a short time, from equilibrium conditions follows from our data.[10] Thus the curves obtained during anodic and cathodic polarisation form loops (Fig. 4, curves *a* and *b*). On the basis of these curves several conclusions can be made concerning the kinetics of the electrochemical adsorption of hydrogen and oxygen. It appears from Fig. 4*a* that the oxygen layer is formed and removed more slowly than the hydrogen layer inasmuch as the direct and reverse curves form a much larger loop at the upper arrest. The potential at which oxidation begins in the case of rapid charging, i.e. at which the upper arrest appears on the charging-curve depends on the density of the charging current. It is evident from Fig. 4*b* that in the presence of Cl′ ions no oxygen layer appears on the platinum during the charging time, i.e. under conditions of the experiment in 1/100 sec., since no upper arrest is observed on the curve. On the other hand, in the absence of Cl′ ions (Fig. 4, curve *a*) an appreciable amount of oxygen is actually deposited on the electrode and removed from it during the same period of time. The inhibition of oxygen adsorption in the presence of Cl′ ions here observed is of importance in explaining the depassivating action of the Cl′ ion on metals. These results point to the conclusion that this action is primarily due to an inhibition of the formation of the passivating oxygen layer in the presence of Cl′ ions. A more detailed investigation [11] has shown that the inhibition of the oxygen adsorption on anodic polarisation sets in beginning with a concentration of Cl′ ions of the order of 0·01-0·001 N. A similar effect of the Cl′ ion has been described in a paper by Hickling.[12]

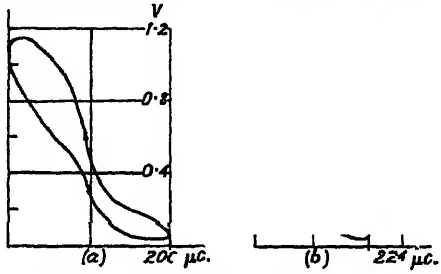


FIG. 4.—A.C. charging-curves at 50 C.P.S.
(*a*) in N. H_2SO_4.
(*b*) in 0·4 N. HCl.

The electrode potential (in volts) referred to the reversible hydrogen potential in the same solution is plotted against the quantity of electricity passed through the electrode. The length of the projection of the curve on the *x*-axis equals the amount of electricity passed during half a cycle, i.e. during 1/100th sec. The upper portions of the curves correspond to the anodic, the lower ones, to the cathodic half-cycle of the alternating current.

The same author has recently published data on charging-curves obtained with a gold electrode at high c.d.'s.[13] In this paper he states that the results obtained by Deborin and Ershler with gold at low c.d.'s [14]

[10] Ershler, *Trans. 2nd Meeting on Metal Corrosion, Acad. Sci., U.R.S.S.*, 1943, **2**, 52.
[11] Ershler, *Thesis* (Moscow, 1941).
[12] Hickling, *Trans. Faraday Soc.*, 1945, **41**, 333.
[13] Hickling, *Trans. Faraday Soc.*, 1946, **42**, 522.
[14] Deborin and Ershler, *Acta Physicochim.*, 1940, **13**, 347.

are not confirmed. As shown in the present paper, however, an agreement of the curves obtained with slow and rapid charging is in general not to be expected. The divergence of such curves in the case of gold points to the fact that various details detected with low densities of the charging current disappear with higher densities in consequence of the slowness of the corresponding processes.

II. Kinetics of the Formation of Adsorbed Layers and of the Dissolution of Metals from Measurements with Alternating Currents.

As stated in the paper by Frumkin, published in the present issue, measurements of the capacity and conductance of an electrode in an alternating current can be used for a direct determination of the velocity of the discharge of hydrogen ions on Pt.[15] The same method may be applied to an investigation of the kinetics of other different electrode processes on the basis of the following considerations. If an electrode is in equilibrium with a solution containing an excess of an indifferent electrolyte and the exchange of the potential-determining substance proceeds at a sufficient rate, then, as has been shown by Krüger [16] the behaviour of an electrode with a surface of 1 cm.^{2} in an A.C. of frequency ω is equivalent to that of a capacity $\overline{C}$ and a conductance $\overline{\Pi}$ connected in parallel, and being determined by the relations

$$\overline{C} = \frac{n^2F^2}{RT} c_0 \sqrt{\frac{D}{2\omega}} + C_1$$

$$\overline{\Pi} = \frac{nF^2}{RT} c_0 \sqrt{\frac{D\omega}{2}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where D is the diffusion coefficient of the potential-determining substance, n its valency, c_0 the concentration of the potential-determining substance in moles per cm.^{3}, C_1 the capacity of the double layer; F, R and T have the usual meaning.

If the surface reaction is slow, Krüger's relations will not be valid. In this case it will, however, still be possible to calculate the values of capacity and conductance of the electrode. Let us give the final results of some calculations of this kind omitting the derivations which will be given elsewhere.

If the discharge reaction $Me^{n+} + ne \rightleftarrows Me$ is slow and J_0 denotes the density of the exchange current, then we find the following relations for the capacity $\overline{\overline{C}}$ and conductance $\overline{\overline{\Pi}}$ of the electrode

$$\overline{\overline{C}} = \frac{2\overline{C}}{1 + 4\omega^2\overline{C}^2r^2} + C_1 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\overline{\overline{\Pi}} = \frac{4\omega^2\overline{C}^2r}{1 + 4\omega^2\overline{C}^2r^2}$$

where

$$r = \frac{1}{\Pi} + \frac{1}{2\overline{\Pi}}$$

$\overline{C}$ and $\overline{\Pi}$ are determined from (1), and

$$\Pi = J_0\frac{nF}{RT}.$$

The last expression is obtained using the ordinary assumptions of the theory of slow discharge. If an ion gives rise to the formation of an

[15] Dolin and Ershler, *ibid.*, 1940, 13, 747; Rosenthal, Dolin and Ershler, *ibid.*, 1946, 21, 213.

[16] Krüger, *Z. physik. Chem.*, 1903, 45, 1.

adsorbed layer, which increases the capacity of the electrode (as compared with the usual value for the double-layer capacity), and the adsorption rate under equilibrium conditions, expressed in electric units, equals J_0 amp./cm.², then we find for the capacity $\overline{\overline{C}}$ and conductance $\overline{\overline{\Pi}}$ of the electrode

$$\overline{\overline{C}} = \frac{C_2}{1 + \omega^2 C_2{}^2 r^2} + C_1 \quad . \quad . \quad . \quad . \quad (3)$$

$$\overline{\overline{\Pi}} = \frac{\omega^2 C^2{}_2 r}{1 + \omega^2 C_2{}^2 r^2},$$

where

$$C_2 = \frac{2C\overline{C}}{2\overline{C} + C}; \quad r = \frac{1}{\Pi} + \frac{1}{2\overline{\Pi}}; \quad \Pi = J_0 \frac{nF}{RT}$$

$\overline{C}$ and $\overline{\Pi}$ being determined by the formulæ (1); C is the equilibrium capacity of the adsorbed layer.

The relations of the capacity and conductance to the frequency and the concentration as given by eqn. (1), (2) and (3) are different.

For example in the case of equation (1) $\overline{\Pi}$ grows proportionally to the square root of the frequency, but is always less than $\omega\overline{C}$. In the case of equation (2) $\overline{\overline{\Pi}}$ tends to a limit with increasing frequency which equals $J_0 \frac{nF}{RT}$, i.e. the density of the exchange current multiplied by $\frac{nF}{RT}$. In the case of rapid adsorption it follows from eqn. (3) that $\omega\overline{\overline{C}}$ and $\overline{\overline{\Pi}}$ increase continuously with the frequency, but $\overline{\overline{\Pi}}$ can exceed $\omega\overline{\overline{C}}$. In the case of slow adsorption equation (3) yields curves, in which again $\overline{\overline{\Pi}}$ tends to a limit, equal to the density of the exchange current at equilibrium, multiplied by $\frac{nF}{RT}$. The latter case is analogous to the one observed in the discharge of H^+ ions on Pt.[15]

From these examples it will be seen that an analysis of the results of measurements conducted in this way permits to determine the role of the diffusion stage and of the electrode reaction rate in the kinetics of the electrode process, as also to measure directly the velocity of the reaction itself under equilibrium conditions if it is not too fast.

Investigations of this kind carried out with mercury in equilibrium with solutions containing mercury ions in different concentrations have shown, that up to a frequency of 5000 C.P.S. and up to a concentration of 0·01 N. $Hg_2(ClO_4)_2$ in a solution containing 2 N. $HClO_4$ the behaviour of the electrode is very well described by equation (1). This shows that the rate of discharge of mercury ions is greater than $\overline{\Pi}$ at $\omega = 5000$ C.P.S. in this equation, multiplied by $\frac{nF}{RT}$ i.e. in the case of 0·01 N. $Hg_2(ClO_4)_2$ greater than 0·04 amp./cm.²,[17]

In the case of a mercury electrode in 2 N. $HClO_4$ containing 0·01 N. HCl the dispersion of the capacity and conductance with frequency was in good agreement with the values calculated by equation (3) if Π was taken equal to ∞. This concordance proves that the adsorption of Cl′ ions on mercury proceeds with a high velocity. The discharge of anions, e.g. hydroxyls on Pt, as has been mentioned above, proceeds, on the contrary, very slowly (see also § III). The difference in the rate of anion discharge on mercury and platinum can be perhaps accounted for by assuming that the discharge of an anion on a metallic atom loosens the bonds between the latter and its neighbours to a certain extent; a discharge of this kind should therefore proceed more slowly on a solid metal. An

[17] Rosenthal and Ershler (unpublished data).

investigation is being conducted at present in this laboratory on the kinetics of the dissolution of a number of metals, as well as on the kinetics of other electrode reactions using the capacity and conductance measurements method.

In a recent paper by Breyer and Gutmann [18] equations are given for the calculation of the capacity and conductance of an electrode, which differ from formula (1). The general applicability of these equations seems, however, to be questionable, in so far as they have been derived from the assumption that at each value of the potential, arising on A.C. charging, a current flows through the electrode equal in strength to the steady state current flowing at this potential. It is easy to show, however, that when currents even of a comparatively low frequency (several C.P.S.) pass through an electrode, steady states are usually not attained and the electrode behaviour should therefore be described by equation (1). Only on very violent stirring of the solution and at very low A.C. frequencies can the relations obtained by Breyer and Gutmann be valid.

III. The Mechanism of Anodic Dissolution and Passivation of Platinum.

A determination of the quantity of adsorbed oxygen from charging-curves may be used for an investigation of the influence of this oxygen on the kinetics of other electrode reaction, e.g. on the kinetics of the dissolution of a metal.

In an investigation of the anodic dissolution of platinum in the presence of Cl′ ions it was shown [19] that the kinetics of this process is controlled by a mechanism of slow discharge. The slowest stage is the interaction of a Cl′ ion and a Pt atom leading to the formation of a Pt—Cl surface complex which weakens the bond between the platinum atom and the lattice of the metal and creates the necessary conditions for the removal of this atom. By rapid oscillographic registration of the charging-curves it was possible to determine the dependence of the rate of anodic dissolution of platinum on the amount of oxygen present on the surface. It appeared that very small amounts of oxygen covering only 6-7 % of the platinum surface reduce the rate of dissolution by a factor of 3 to 4. Thus, in this case, passivation cannot be attributed to the formation of an oxide layer insulating the metal from the solution. A possible explanation of the passivating action of the oxide layer in this case can be given assuming that the retardation of dissolution is due to a change in the electric field of the double-layer when adsorbed oxygen atoms appear. The direction of this field is such that it should hinder the formation of the Pt—Cl complex, i.e. should retard the slowest stage of the dissolution.

The existence of an electric field produced by adsorbed oxygen atoms at the Pt-solution-interface was shown before by direct experiment,[4, 5] in which case a desorption of anions from the double-layer was observed when an adsorbed layer of oxygen was formed.

Summary.

Charging-curves obtained at high c.d.'s permit the investigation of the kinetics of electrode reactions. It has been shown that the formation of an adsorbed layer of oxygen on Pt proceeds much more slowly than the formation of an adsorbed layer of hydrogen. The adsorption of oxygen is retarded in the presence of Cl′ ions. The difference in the behaviour of gold when charged with low and high c.d.'s has been accounted for.

[18] Breyer and Gutmann, *Trans. Faraday Soc.*, 1946, **42**, 645, 650.
[19] Ershler, *Compt. rend. U.R.S.S.*, 1942, **37**, 258, 262; *Acta Physicochim.*, 1944, **19**, 139.

In the case of strong adsorption of oxygen on Pt, Ag and Au a change of adsorption properties of the metal surface is observed, which is preserved after the removal of firmly bound oxygen. The strength of the bond between adsorbed oxygen and metals increases with time and with the temperature of oxidation.

A.C. measurements of the capacity and conductance of an electrode in equilibrium with a solution at different frequencies permit the investigation of the kinetics of different electrode reactions.

By means of such measurements it has been shown that the dissolution of mercury as well as the adsorption of Cl′ ions on its surface proceeds with a high velocity. The reasons of the difference in the rate of adsorption of anions on mercury and platinum have been discussed.

Data concerning the influence of adsorbed oxygen on the rate of anodic dissolution of platinum are given.

Résumé.

La formation de couches d'hydrogène et d'oxygène, adsorbées sur Pt, Ag et Au, a été étudiée d'un point de vue cinétique au moyen (1) de courbes de charge à hautes densités de courant et (2) de mesures, en courant alternatif à différentes fréquences, de la capacité et de la conductance d'une électrode en équilibre avec une solution. Les mécanismes de la dissolution et de la " passivation " anodiques du platine sont aussi considérés en fonction de la quantité d'oxygène adsorbé, que l'on calcule à partir des courbes de charge.

Zusammenfassung.

Die Kinetik der Bildung von Adsorbatschichten von Wasserstoff und Sauerstoff an Pt, Ag und Au wurde auf zwei Weisen untersucht, u.zw. (*a*) durch Aufladungskurven bei hohen Stromdichten und (*b*) Wechselstrommesungen, bei verschiedenen Frequenzen, der Kapazität und Leitfähigkeit einer Elektrode, die mit einer Lösung im Gleichgewichtszustand ist. Der Mechanismus der anodischen Auflösung und Passivierung von Platin wird mit Bezug auf die aus den Aufladungskurven berechnete Menge des adsorbierten Wasserstoffs besprochen.

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THE ANODIC BEHAVIOUR OF METALS. PART IV. SILVER.

BY A. HICKLING AND D. TAYLOR.

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In continuation of the work previously reported,[1] the anodic polarisation of silver has now been investigated by the oscillographic method which records the variation of potential with quantity of electricity passed prior to oxygen evolution. No previous work on silver from the present standpoint has been published, but other methods of investigation have yielded some information. Luther and Pokorny[2] obtained an extensive silver

[1] Hickling, *Trans. Faraday Soc.*, 1945, **41**, 333; 1946, **42**, 518; Hickling and Spice, *ibid.* (in course of publication).

[2] *Z. anorg. Chem.*, 1908, **57**, 290; see also Rollet, *Compt. rend.*, 1928, **186**, 748.

surface by plating the metal on to platinised platinum, and this was polarised anodically at a small constant current in N. NaOH and a graph of potential against time obtained. Under these circumstances the polarisation was very prolonged, and two definite arrests prior to oxygen evolution were observed. From a knowledge of the amount of silver present and the quantities of electricity passed at each stage it was concluded that the silver was first oxidised quantitatively and reversibly to Ag_2O, and this in turn to Ag_2O_2, no higher oxide being formed before oxygen was evolved; it was suggested that in acid solution and in the electrolysis of solutions of silver salts a higher oxide, possible Ag_2O_3, might be anodically produced. The anodic products obtained in the electrolysis of solutions of silver salts have been examined by numerous investigators;[3] in general peroxy-salts, the constitutions of which have been variously interpreted, are obtained, but there is some evidence that they contain a higher oxide than Ag_2O_2, and it has been suggested that this may also be formed in alkaline solution under special conditions.[4]

Experimental.

The electrical circuit and the electrolytic cell employed were fundamentally as previously described.[1] The electrical circuit was, however, modified slightly by the addition of appropriate switching arrangements so that the time base and charging circuit could be operated independently. In this way, in addition to the usual repetitive anodic and cathodic tracks showing directly the variation of potential with quantity of electricity passed, single sweep tracks of potential against time could be obtained for anodic and cathodic polarisations and for the decay of potential after polarisation of the electrode. These single sweep tracks were found to have a limited application in assisting the interpretation of the repetitive tracks which are the more generally useful. The silver electrodes used were made by plating silver from a cyanide bath, in the form of a smooth coating *ca.* 0·004 in. thick, on to a platinum wire electrode of area 0·025 sq. cm. sealed into the end of a glass tube. One plating served for 3 or 4 experiments, the electrode being cathodically cleaned after each experiment. Observations have been made mainly with N. NaOH as electrolyte; additional observations have been carried out in a variety of buffer solutions. Except where otherwise stated, all experiments were made at 18° C., using air-free solutions in an atmosphere of nitrogen.

In general the results are shown as photographed oscillograms in which the ordinates represent potentials and the abscissæ are proportional to quantities of electricity passed. Suitable horizontal reference lines at intervals of 0·25 V. were photographed immediately after recording the polarisation tracks, so that significant potentials can be read directly from the oscillograms. The quantity of electricity passed at any stage in the polarisation is computed from the known capacity of the condenser used in series with the electrolytic cell and the horizontal displacement which is governed by the voltage to which the condenser is charged (on the original photographs, before reduction, 1 V. on the condenser corresponds to an average horizontal displacement of *ca.* 1 mm.). Except where otherwise stated, a 6·1 μF condenser was used in series with the cell. All potentials quoted are on the hydrogen scale.

Results.

Behaviour in Alkaline Solution.—In Plate I, A, is shown the characteristic oscillogram in N. NaOH for the anodic polarisation of silver at 18° C.

[3] For a survey with full references of the very extensive early literature, see Brown, *J. Physic. Chem.*, 1916, **20**, 680; also Weber, *Trans. Electrochem. Soc.*, 1918, **32**, 391.

[4] See Jirsa, *Z. Elektrochem.*, 1919, **25**, 146; Jirsa and Jelinek, *Z. anorg. Chem.*, 1926, **158**, 61.

To face page 78

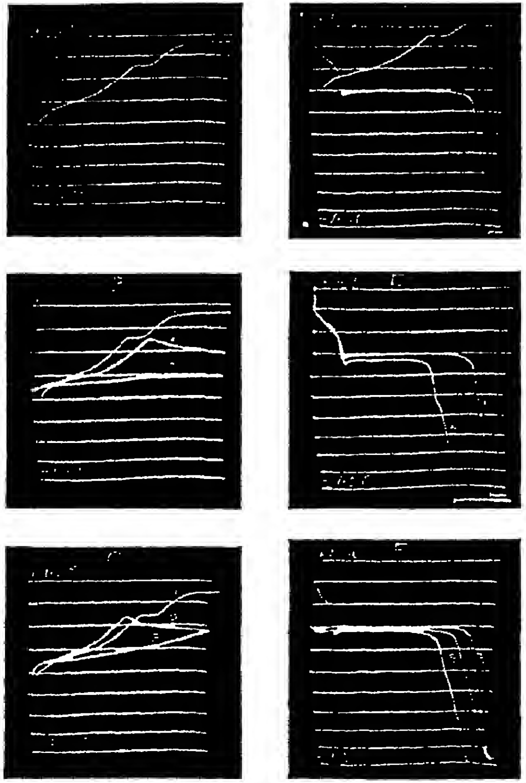

PLATE I.

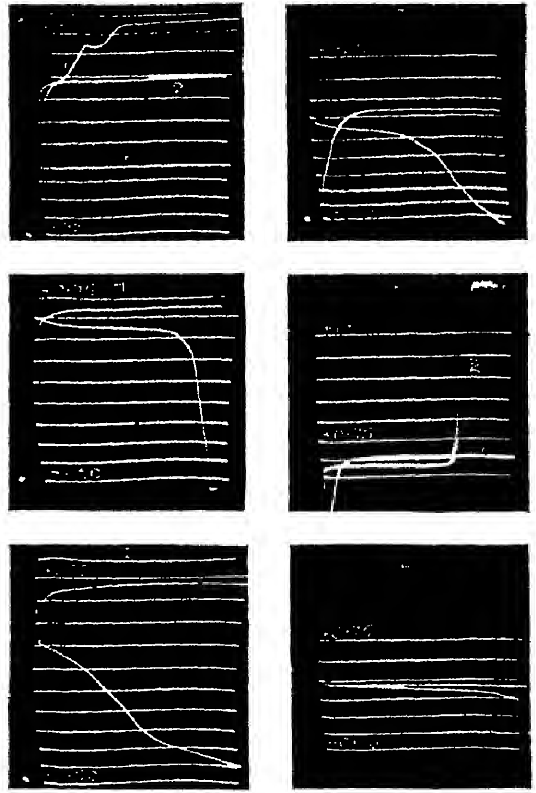

PLATE II.

with a polarising c.d. of 0·04 amp./sq. cm. The spot on the extreme left of the photograph indicates the steady oxygen evolution potential at the same c.d. It may be noted that a very rapid initial build-up of potential is followed by two main steps or arrests, the potential ultimately rising to the oxygen evolution value. The oscillogram was found to change only very slightly with time of electrolysis, and was satisfactorily reproducible. Stirring of the electrolyte did not affect the polarisation track. In contrast to the metals previously studied,[1] c.d. and temperature markedly influenced the nature of the track. In Plate I, B, is shown the anodic track at three different c.d.'s of 0·04, 0·016 and 0·008 amp./sq. cm. severally, the oscillograms being marked 1, 2 and 3, in order of decreasing c.d. It is seen that at 0·016 amp./sq. cm. the potential never rises to the oxygen evolution value, but having reached the arrest immediately prior to this it actually decreases with increasing quantity of electricity passed, while at 0·008 amp./sq. cm. the potential does not rise beyond the previous step. Increase of temperature had an effect very similar to that of decreasing c.d., and this is illustrated in Plate I, C, in which are shown the anodic tracks at 18, 40 and 80° C., marked 1, 2 and 3 severally, the c.d. in each case being 0·04 amp./sq. cm. Anodic prepolarisation had only a very slight effect on the oscillogram in alkaline solution tending rather to lengthen the steps in the curves.

In Plate I, D, are shown the anodic and cathodic polarisation tracks at a c.d. of 0·04 amp./sq. cm. photographed together. It is seen that the cathodic track shows two arrests, the first relatively short and not very well defined, while the second lower step extends over most of the track and occurs at a practically steady potential. Increase of c.d. tended to shorten the lower step as is shown in Plate I, E, in which two cathodic tracks at 0·04 (1) and 0·1 amp./sq. cm. (2) are displayed together. At very low c.d.'s, the long step in the cathodic track showed occasional V-shaped valleys, the phenomenon being rather what might be expected if successive layers of some anodic product were being reduced. In Plate I, F, are shown cathodic tracks at 18, 36 and 54° C. (numbered 1, 2 and 3 severally), the c.d. in each case being 0·04 amp./sq. cm. Rise of temperature tends to eliminate the upper step in the track, and lengthens the lower one. Anodic prepolarisation was found to increase the length of the lower step, but the effect was very transient and rapidly disappeared.

The influence of various anions in alkaline solution was ascertained by using N. NaOH electrolytes which had been made 0·05 M. with respect to the sodium salts of various acids. Carbonate, borate, phosphate, nitrate, sulphate and fluoride were without effect. Chloride, bromide and iodide gave oscillograms indicating that the silver was being attacked to form the appropriate halide, the potential remaining steady in the vicinity of the reversible value expected for an electrode of silver in a saturated solution of the appropriate silver halide. The presence of NH_4OH was found to have considerable influence on the anodic polarisation track in alkaline solution. This is illustrated in Plate II, G, which shows the ordinary track in N. NaOH (1), and in the same solution made 0·05 M. with respect to NH_4OH (2); a c.d. of 0·02 amp./sq. cm. and a series condenser of 15·1 μF capacity were used in these experiments. In the presence of NH_4OH it is noted that the potential never rises from that corresponding to the first main step.

Behaviour in Buffer Solutions.—The effect of decrease of *p*H value on the anodic behaviour of silver was investigated using a variety of buffer and acid solutions as electrolytes. Except where otherwise stated, a c.d. of 0·04 amp./sq. cm. and standard conditions were used throughout these experiments. In Plate II, H, are shown the anodic and cathodic tracks in N. Na_2CO_3 (approx. *p*H 12); the anodic tracks shows that, with the quantity of electricity passed, the potential never rises beyond the customary first oxidation step in the polarisation, and the cathodic track

indicates merely the corresponding reduction. By using the single sweep circuit, and passing sufficient electricity, it was found possible to force the potential to the oxygen evolution value and the total polarisation track obtained was fundamentally similar to that observed in N. NaOH but with the first step greatly extended. In 0·1N. $Na_2B_4O_7$ (approx. pH 9·2) the behaviour was similar to that in the carbonate solution but it appeared that some dissolution of metal to form an insoluble borate was also probably occurring. Thus in Plate II, I, are shown the customary repetitive anodic and cathodic tracks; observations at different c.d.'s showed a displacement of potential in the tracks indicating the existence of some surface resistance at the electrode, and the cathodic track did not exhibit the usual well-defined step. Using the single sweep circuit it was possible to force the potential to the oxygen evolution value, but the track was then enormously extended. In 0·2 M. KH_2PO_4 + 0·2 M. Na_2HPO_4 (approx. pH 6·8) oxidation of the silver appeared to have been replaced completely by metal dissolution. The repetitive anodic and cathodic tracks are shown in Plate II, J; an anodic process sets in at approx. + 0·5 v. and can apparently continue almost indefinitely. The potential is in agreement with the reversible value of + 0·53 v. obtained for a silver electrode immersed in the phosphate buffer to which a few drops of silver nitrate had been added, and apparently represents merely the potential of silver against a saturated solution of silver phosphate. By prolonged anodic prepolarisation in the phosphate buffer the track (2) shown in Plate II, K, was obtained; the ordinary track (1) is also included for comparison. It is seen that after prolonged anodic prepolarisation the potential can be made to rise towards the oxygen evolution value, but this section of the curve is very indefinite, the potential being quite unsteady, and suggests the existence of a thick poorly-protective film on the electrode; a brown film which readily broke away was indeed observed. In yet more acid solutions, the oscillograms indicated that the sole anodic process was the dissolution of silver and the corresponding cathodic process the discharge of silver ions. A typical example is shown in Plate II, L, which gives the anodic and cathodic tracks in N. HCl; both anodic and cathodic processes occur at a potential of + 0·23 v. which is in good agreement with the reversible static potential of + 0·22 v. obtained for a silver electrode immersed in N. HCl saturated with AgCl.

Measurement of the Oxide Potentials of Silver.—Values are quoted in the literature for the oxide potentials of silver, but these have generally been inferred from the static potentials of silver after anodic oxidation rather than determined by setting up independently the equilibrium systems. Thus Luther and Pokorny [3] give values for the oxide potentials in N. NaOH which corrected to the hydrogen scale are as follows: Ag/Ag_2O + 0·38 v., Ag_2O/Ag_2O_2 + 0·61 v., Ag_2O_2/Ag_2O_3 (?) + 0·78 v. In the present work an attempt has been made to establish the potentials independently. Ag_2O was prepared by precipitation, washed and dried; it was then mixed with finely powdered silver, shaken up with the chosen electrolyte, a short platinum electrode wholly immersed in the sludge formed, and the potential measured against a saturated calomel electrode. Under these conditions the following values, expressed on the hydrogen scale, were obtained:

Electrolyte	N. NaOH	N. Na_2CO_3	0·1N. $Na_2B_4O_7$
Ag/Ag_2O Potential	+ 0·40	+ 0·52	+ 0·67 v.

The potentials in N. NaOH and N. Na_2CO_3 were very steady and reproducible, but that in 0·1 N. $Na_2B_4O_7$ fell off with time. Pure Ag_2O_2 was prepared by Watson's method,[5] mixed with a little Ag_2O, and the potential in N. NaOH measured as above; a steady and reproducible value of + 0·63 v. on the hydrogen scale was obtained. No reliable method for

[5] *J. Chem. Soc.*, 1906, 89, 578.

the preparation of any higher oxide of silver in a pure state appears to exist, but the black product obtained on anodic oxidation of silver nitrate with a platinum anode is alleged to contain a higher oxide, possibly Ag_3O_4. A quantity of this product was therefore prepared, washed with water and N. NaOH in the cold, and its potential in N. NaOH then measured as above. The freshly prepared product gave a reproducible value of + 0·79 v. on the hydrogen scale which decreased slowly with time; on adding Ag_2O the potential dropped fairly rapidly to the vicinity of the value of + 0·63 v. observed for Ag_2O_2.

Measurement of the True Area of the Silver Electrode.—To obtain an idea of the ratio, accessible area/apparent area, for the silver electrode used, the method of Bowden and Rideal [6] was employed in which the double layer capacity of the metal when used as a cathode in acid solution is measured and compared with that of mercury for which the accessible area may be assumed to be the same as the apparent area. Using the direct method of measurement,[7] the capacity of the silver electrode in N. H_2SO_4 immediately prior to hydrogen evolution was found to have an average value of 126 μF per apparent sq. cm., while amalgamated electrodes under the same conditions had an average capacity of 10·9 μF per apparent sq. cm. If these values are accepted, the indication is that the true area of the silver electrode is about 11·5 times its apparent area. As a check on this, the capacity of a silver electrode, prepared in the usual way, was measured by a quite different method in which A.C. of low amplitude was superimposed on a direct polarising current and the fluctuation of potential between the silver cathode and a reference electrode was applied after amplification to the *Y*-deflecting plates of a cathode ray oscillograph; the deflection produced was compared with those obtained by application of the same alternating current to a series of standard capacities, and the unknown obtained by interpolation. This method gave a minimum value of 102 μF per apparent sq. cm. for the capacity of the silver electrode immediately prior to hydrogen evolution, and 11·7 μF per apparent sq. cm. for a liquid mercury electrode under the same conditions. If these values are accepted, it would appear that the true area of the silver electrode is about 8·7 times its apparent area. Taking into account the difficulty of reproducing exactly a metallic surface, the agreement between the results by the two methods is fairly satisfactory, and it can be taken, probably without substantial error, that the true area of the silver electrodes used in the present work is about ten times their apparent area.

Discussion.

The oscillograms show that silver in alkaline solution gives a characteristic anodic polarisation track, the form and extent of which is, however, markedly dependent upon c.d. and temperature. Under conditions such that the oxygen evolution potential is attained, several stages in the anodic polarisation can be detected:

(1) A rapid, probably linear, rise of potential constituting the initial section of the track.
(2) A long step in which the potential rises slowly and non-linearly; there is some suggestion of a subsidiary step at the beginning of this stage.
(3) A shorter well-defined step from which the potential rises ultimately to that of oxygen evolution.

By analogy with the previous metals studied,[1] it appears probable that stage (1) corresponds to the charging of a double layer. This section of the oscillograms was so steep that it was not possible to obtain any very

[6] *Proc. Roy. Soc. A*, 1928, **120**, 80. [7] See Hickling and Spice, *loc. cit.*[1]

precise measure of this double layer capacity, but such measurements as could be made indicated that it was in the region of 1300 μF per apparent sq. cm. of silver surface. Allowing for the fact that the real area of the surface is about 10 times its apparent area, this value is of the same general order as that found for other metals.[1]

Stage (2) is clearly defined in the oscillograms and commences in N. NaOH at a potential of + 0·40 V., and in N. Na_2CO_3 at + 0·50 V.; in 0·1 N. $Na_2B_4O_7$ the potential was found to vary with the current used, suggesting the presence of some resistance at the surface of the electrode, but by working at different currents and extrapolating to zero, the value of + 0·65 V. was obtained. As discussed in the experimental section, the static reversible Ag/Ag_2O potentials in these three solutions are +0·40, + 0·52 and + 0·67 V. severally. The close agreement between these two sets of values strongly suggests that the onset of stage (2) corresponds to the formation of Ag_2O on the silver surface, and the observations in the presence of NH_4OH, in which Ag_2O is soluble, are in conformity with this view. As shown by the oscillograms the extent of stage (2) depends very markedly on the experimental conditions; thus this stage is extended by decrease of c.d., rise of temperature, and decrease of pH value. The quantity of electricity passed in stage (2) can be estimated approximately from the oscillograms, and in N. NaOH at 18° C. with a polarising c.d. of 0·04 amp./sq. cm. it is found to be about 7500 microcoulombs per apparent sq. cm. of silver surface; this is sufficient to liberate approximately 23×10^{15} atoms of oxygen. Taking the specific gravity of silver as 10·5, the diameter of the silver atom may be calculated to be approximately $2{\cdot}6 \times 10^{-8}$ cm., and hence there would be about $1{\cdot}5 \times 10^{15}$ atoms of metal per true sq. cm. or 15×10^{15} atoms of metal per apparent sq. cm. at a silver surface, assuming the measured value of 10 for the ratio accessible area/apparent area to be substantially correct. Hence under the usual conditions in N. NaOH the quantity of electricity passed in stage (2) is sufficient to provide for a layer of Ag_2O approximately 3 molecules in thickness. At lower c.d.'s or higher temperatures the quantity of electricity passed in stage (2) is increased, indicating presumably a greater thickness of the Ag_2O film. The cathodic polarisation tracks serve to confirm these conclusions. The lower well-defined step begins at a potential of about + 0·25 V., appreciably more negative than the reversible Ag/Ag_2O value, and its extent is approximately the same as that of stage (2) in the anodic polarisation, and it depends upon experimental conditions in the same way; it would thus appear to represent the reduction of Ag_2O. Additional evidence in support of this was obtained by oxidising a silver sheet anodically until it became covered with Ag_2O, and then immersing it in N. NaOH and measuring its potential while bubbling hydrogen around it; initially the potential was + 0·40 V., but it fell rapidly in the hydrogen atmosphere to the region of + 0·3 to + 0·2 V. where it remained for some hours before ultimately falling to a negative value. The general conclusion reached, therefore, is that in the anodic polarisation of silver in alkaline solution, following the charging up of the double layer, there occurs the formation of a film of Ag_2O the process beginning at the reversible Ag/Ag_2O potential; it seems that this film (unlike the previous cases studied [1]) is porous and of little protective power and it can therefore grow to a considerable thickness, even in the initial stages of polarisation. Any factor tending to increase rate of reaction or diffusion, such as rise of temperature, or to diminish rate of oxygen accumulation, such as decrease of c.d., tends to increase the thickness of the film. It has been pointed out above that there is some suggestion of a subsidiary step at the beginning of stage (2) in the polarisation, occurring at a slightly lower potential and of very short duration. It is not sufficiently well-defined to permit of identification, nor does it appear separately in the cathodic tracks; it may represent some adsorption of oxygen prior to Ag_2O production, or conceivably

the incipient formation of a silver suboxide the existence of which has been reported.[8]

The characteristics of stage (3) in the anodic polarisation track are of great interest. At high c.d.'s at room temperature it appears as a well-defined flat step at + 0·88 v. in N. NaOH passing ultimately into oxygen evolution. The quantity of electricity passed from the beginning of the step to the point where the potential approaches the oxygen evolution value can be estimated approximately from the oscillograms, and *where the step is completed* it has a fairly definite value of about 4500 microcoulombs per apparent sq. cm. This is sufficient to liberate approximately 14×10^{15} atoms of oxygen, or approximately 1 atom of oxygen for each atom of silver in the surface. Since the silver has previously been oxidised to Ag_2O, these figures would correspond roughly to the formation of a unimolecular film[9] of Ag_2O_3, but too much importance cannot be attached to this result since the data are necessarily somewhat uncertain. The potential of stage (3) is very definite at + 0·88 v. which is much higher than the Ag_2O/Ag_2O_2 potential of + 0·63 v., and is most nearly approached by the potential set up by the silver peroxynitrate product which was measured as + 0·79 v. It appears certain, therefore, that stage (3) in the anodic polarisation represents the formation of an oxide of silver containing more oxygen than Ag_2O_2, and possibly to be represented as Ag_2O_3 although the evidence on this point cannot be considered conclusive. At low c.d.'s or high temperatures the potential may rise to that of stage (3) in the anodic polarisation, but then falls with increasing quantity of electricity passed, giving a characteristic peak in the oscillogram. This seems unmistakably to indicate that the polarisation leads primarily to this higher oxide, but under the conditions of its formation it is unstable and decomposes. To examine this decomposition, the decay of potential at an anodically polarised silver electrode on open circuit was investigated both using the cathode ray oscillograph, and more precisely by using an interrupter and thyratron-potentiometer technique.[10] The results were in all cases the same; after a short arrest beginning at about + 0·88 v., the potential fell rapidly to + 0·63 v. —the value for the Ag_2O/Ag_2O_2 electrode—and thereafter decreased very slowly. The general conclusion to be drawn would therefore seem to be that in the anodic polarisation of silver in alkaline solution Ag_2O is first formed in a film the thickness of which depends upon the experimental conditions, and that the next stage of oxidation is the formation of a higher oxide containing more oxygen than Ag_2O_2, possibly Ag_2O_3, which, however, decomposes to give the dioxide. This decomposition probably proceeds by interaction with the monoxide previously formed, e.g. $Ag_2O_3 + Ag_2O = 2Ag_2O_2$, and in conformity with this it may be noted that addition of Ag_2O to the silver peroxynitrate product brought about a fall in potential (*vide supra*). It is to be emphasised that there is no arrest at + 0·63 v. in the anodic polarisation curves, indicating that Ag_2O_2 is not *primarily* formed in the anodic polarisation but arises purely as a secondary product.[11] The cathodic polarisation tracks are in agreement with the general conclusion reached. They show an upper step extending from about + 0·75 to + 0·50 v. which probably represents the

[8] See Mellor, *Comprehensive Treatise*, Vol. III, p. 368.

[9] This result would suggest that of the Ag_2O previously formed only the unimolecular layer in immediate contact with the silver surface is oxidised to Ag_2O_3.

[10] See Hickling and Salt, *Trans. Faraday Soc.*, 1941, 37, 450, for details of the method. The observations mentioned were made as part of a general study of the decay of oxygen overvoltage which will be published later.

[11] Luther and Pokorny[2] concluded that Ag_2O_2 was primarily formed, but their experimental method served only to detect the anodic products present after an appreciable time. A close examination of their results actually shows a peak in their polarisation curves representing the decay of some higher oxide initially formed (as found in the present work) but they did not comment on this.

reduction of Ag_2O_2 and any higher oxide as yet undecomposed to Ag_2O_2; at higher temperatures this step disappears indicating that all oxides higher than Ag_2O, if formed, have been decomposed.

The remarks so far made apply to the behaviour of a silver anode in NaOH solution. In a N. Na_2CO_3 electrolyte the anodic process appears to be fundamentally the same, but the step representing the formation of Ag_2O is greatly extended. In 0·1 N. $Na_2B_4O_7$ the main anodic process appears to be the formation of silver monoxide, probably accompanied by the production of silver borate, and the potential can only rise with difficulty to the oxygen evolution value; the track is then so extended that it is impossible to distinguish any intermediate stages with certainty. In yet less alkaline solutions the silver never becomes satisfactorily passive, and the anodic and cathodic processes as indicated by the oscillograms are merely the dissolution of silver and its deposition.

The authors' thanks are due to Mr. S. Hill for making the measurements on the decay of potential by the interrupter and thyratron-potentiometer technique.

Summary.

1. The initial build-up of anodic polarisation at a silver anode over a wide range of conditions has been investigated using the cathode ray oscillograph.

2. In NaOH solution three main stages in the polarisation have been distinguished: they are (*a*) the charging of a double layer, (*b*) the formation of Ag_2O in a film the thickness of which depends upon the experimental conditions, and (*c*) the formation of an oxide of silver higher than Ag_2O_2 which decomposes to give the latter substance. Ag_2O_2 is not primarily formed in the polarisation, but arises as a secondary product.

3. With progressively decreasing alkalinity of electrolyte the anodic polarisation at first remains fundamentally the same as in NaOH but with increased formation of silver monoxide, but from the region of *p*H 9 downwards a silver anode does not become satisfactorily passive and the anodic process is merely the dissolution of silver.

Résumé.

(1) La toute première formation d'une polarisation anodique à une anode d'argent a été étudiée au moyen de l'oscillographe cathodique dans des conditions très variées.

(2) Dans des solutions de NaOH, on a distingué trois stades principaux dans la polarisation : (*a*) la charge de la double couche, (*b*) la formation d'un film de Ag_2O, dont l'épaisseur dépend des conditions expérimentales et (*c*) la formation d'un oxyde d'argent supérieur à Ag_2O_2 et qui se décompose pour donner ce dernier. Ag_2O_2 n'est pas un produit primaire de la réaction, mais un produit secondaire.

(3) Avec une alcalinité progressivement décroissante de l'électrolyte, la polarisation anodique demeure tout d'abord fondamentalement la même que dans NaOH, seulement avec une formation accrue de monoxyde d'argent, mais pour des *p*H inférieurs à 9, une anode d'argent ne devient pas passive de façon satisfaisante et le processus anodique est alors simplement la dissolution de l'argent.

Zusammenfassung.

(1) Das anfängliche Anwachsen der anodischen Polarisation einer Silberanode wurde unter ganz diversen Bedingungen mit Benützung eines Kathodenstrahloszillographen untersucht.

(2) In NaOH-Lösungen sind drei Stufen im Polarisationsvorgang ausnehmbar: (*a*) die Aufladung einer Doppelschicht, (*b*) die Bildung

eines Ag_2O—Films, dessen Dicke von den Versuchsbedingungen abhängt, und (c) die Bildung eines Oxyds höher als Ag_2O_2, das sich in das letztere Oxyd umsetzt. Ag_2O_2 selbst ist nicht ein primäres Produkt bei der Polarisation, sondern entsteht als sekundäres Produkt.

(3) Bei abnehmender Alkalinität des Elektrolyts bleibt die anodische Polarisation zunächst im grossen und ganzen am selben Wert wie für NaOH, aber die Bildung von Silbermonoxyd nimmt zu. Dagegen wird im Gebiet, wo der *p*H-Wert kleiner als 9 ist, die Anode nicht genügend passiv und der anodische Vorgang ist lediglich die Auflösung von Silber.

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THE DISCHARGE OF THE ZINC-LEAD DIOXIDE CELL.

BY W. H. BECK AND W. F. K. WYNNE-JONES.

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1. Introduction.

In the previous paper an account has been given of various experimental conditions in the preparation of the lead dioxide electrode and the effect of these variations on the capacity of the zinc-lead dioxide cell when discharged under standard conditions. In that investigation our aim was to discover how the capacity of the cell depended on the conditions of discharge, when the lead-dioxide electrode was prepared by a standard procedure. In this work, the effects of varying the nature of the cell electrolyte, its temperature, and the rate of discharge have been examined. It has been found that the capacity of the cell depends on all these factors. We have also examined, at a single temperature, lead-dioxide electrodes prepared by an entirely different method, namely, anodic deposition from aqueous lead nitrate, but for this electrode we have used sulphuric acid, and a few acids giving soluble lead salts. In this case also, the capacity of the cell was found to depend on the rate of discharge.

2. Experimental.

2. 1. Method.

2. 1.1.—The cell was discharged through fixed resistances of different values to give varying rates of discharge. The discharge was followed by observing the change in cell voltage with time. The voltage was measured on a Cambridge Unipivot millivoltmeter (with a suitable series resistance). The meter was frequently calibrated against an accurate potentiometer, and could be read to $\pm$ 0·004 V. The voltage changes in the first few seconds of discharge were followed photographically on a Cossor double-beam oscilloscope with a D.C. amplifier. The external resistance across the cell terminals was measured with an accuracy of 0·1 % on a post-office box. Time was measured on an electric clock run off the A.C. mains, and could be estimated to the nearest second. Discharge was started by dropping the dry zinc and lead dioxide electrodes into the cell electrolyte.

2. 1.2.—The capacity of the cell per sq. cm. of surface was calculated from the area in volt-seconds under the voltage-time curve for the discharge, between the time ordinates $t = 0$, and $t =$ the life of the cell, divided by the external resistance in ohms, and the apparent area of the

oxide electrode in $cm.^2$. The life of the cell was taken to be the time for which the cell voltage remained above 75 % of its maximum value. Beyond this time, the voltage fell very rapidly to a value not characteristic of the normal zinc-lead dioxide cell. The mean c.d. of discharge for a particular value of the external resistance was calculated as the capacity divided by the life, and is expressed in $ma./cm.^2$ of apparent surface of the oxide electrode. The maximum c.d. for a particular value of the external resistance is simply the maximum cell voltage divided by the product of the external resistance and the apparent area of the oxide electrode.

2. 2. Preparation of the Lead Dioxide Electrodes.

2. 2.1.—The two types of oxide electrode will be referred to as types I and II. Type I, which was specially stabilised for this work, was prepared as follows.

A smooth, fine-grained layer of lead, 0·0025 cm. thick was deposited on a suitable base from a lead perchlorate solution containing 5 % lead, 5 % free perchloric acid, and 0·25 % peptone by weight.[1] The bath was run at 18° c., pure lead anodes were employed, and the deposition was continued for 20 min. at a c.d. of 2 $amp./dm.^2$ at the cathode. The lead deposit was now thoroughly washed in cold water, rinsed with alcohol, and dried in a current of air at 60° c. An area of 5 sq. cm. of the lead deposit was now oxidised in the following manner.

(*a*) Oxidised for 15 min. at 2 $amp./dm.^2$ in a solution containing 100 g. Na_2SO_4, and 11 g. $KClO_4$ per litre, at 18° c.; washed for 1 min. in running cold water.

(*b*) Reduced for 3 min. at 2 $amp./dm.^2$ in normal sulphuric acid.

(*c*) Reoxidised for 15 min. at 2 $amp./dm.^2$ in normal sulphuric acid; washed for 1 min. in running cold water, rinsed with alcohol, and dried in a current of air at 60° c.

In this way one obtains a layer of oxide with an average thickness of about 0·002 cm., consisting of very finely divided lead dioxide of a dark-brown colour, with a few minute, white specks. The capacity of these electrodes measured under standard conditions (by discharging against amalgamated zinc in 30 % sulphuric acid through a fixed resistance of 32 ohms), was sufficiently reproducible for the present work. The order of reproducibility is illustrated by the capacities of 24 electrodes discharged under the standard conditions. The mean capacity was 5·00 $coulombs/cm.^2$ with a R.M.S. deviation of $\pm$ 2·2 % and of the 24 electrodes, 20 had capacities within the range 4·89-5·11 $coulombs/cm.^2$, the remaining four having the capacities 4·65, 4·81, 4·86 and 5·18 $coulombs/cm.^2$.

2. 2.2.—The bath used in preparing type II was an aqueous solution of lead nitrate (410 g. to 1 litre of water), containing a suspension of finely ground yellow litharge, to maintain a constant concentration of lead in the bath. The bath was run at 30° c., with an anode c.d. of 3·3 $amp./dm.^2$. The cathode was of pure lead, and the anode on which the lead dioxide was deposited was of steel which was previously etched for 5 min. in a mixture of 1 part by volume of concentrated nitric acid to 3 parts water at approximately 3° c. The deposition of lead dioxide under these conditions was 100 % efficient, so that the amount of electricity passed was a direct measure of the amount of lead dioxide precipitated at the anode. In the present case, the electrodeposition was continued for 7 min. corresponding to a theoretical capacity of the oxide electrode of 13·9 $coulombs/cm.^2$.

This type of electrode differs markedly from type I in appearance. It is of a blue-grey colour, and has a pronounced sheen. It is very hard and compact in contrast to the soft, porous nature of the formed type of deposit, and in fact strongly resembles a good electrodeposit of metal.

[1] Mathers, *Trans. Amer. Electrochem. Soc.*, 1910, **17**, 261.

2. 3. The Cell Electrolytes.

2. 3.1.—The discharge of the zinc-lead dioxide cell in which the oxide electrode was of type I was examined at two temperatures 18° and −18° C., in three electrolytes, sulphuric acid (A), hydrochloric acid containing phosphoric acid (B), and hydrochloric acid of the same concentration as in (B), but containing a higher concentration of phosphoric acid (C). The phosphoric acid in electrolytes (B) and (C) was added to cut down the solubility of lead in these solutions. Electrolyte (A) could be regarded as a normal electrolyte in which only electrochemical action can occur, (B) and (C) as abnormal solutions in which chemical as well as electrochemical action can and did, in fact, occur. The chemical action which took place was the oxidation of the hydrochloric acid to chlorine by the lead dioxide. The composition of the three solutions was as follows.

Electrolyte A.	Sulphuric acid	367·5 g./l.
	Mercuric chloride	10·0 g./l.
Electrolyte B.	Orthophosphoric acid	687 g./l.
	Hydrochloric acid	27·8 g./l.
	Mercuric chloride	20·0 g./l.
Electrolyte C.	Orthophosphoric acid	1005 g./l.
	Hydrochloric acid	27·8 g./l.
	Mercuric chloride	20·0 g./l.

The mercuric chloride was added to each electrolyte in order to amalgamate the zinc electrode. This served to cut down the irreversible chemical reaction between the zinc and the electrolytes. The results were the same if the zinc was amalgamated before immersion in the electrolyte, apart from a small effect on the cell voltage.

2. 3.2.—The discharge of the zinc-lead dioxide cell in which the oxide electrode was of type II was examined at 18° C., in normal sulphuric acid. In these experiments, no mercuric chloride was added to the cell electrolyte, but the zinc electrodes were pre-amalgamated in a saturated solution of mercuric chloride.

2. 4. Temperature.

For the experiments at − 18° C., the beaker containing the electrolyte was placed in a freezing-mixture of ice and sulphuric acid which was renewed every 7 min. if necessary. No attempt was made to cool the electrode down to − 18° C., before bringing them into contact with the cell electrolyte at that temperature, but the temperature of the solution was not observed to rise when the electrodes had been immersed.

2. 5. The Resistance of the Dry Lead Dioxide Electrode of Type I.

The resistance of the dry lead dioxide electrode of type I to which reference is made later, was measured by a method similar to that used in measuring the electrical resistance of powders. The electrode was placed between two highly polished brass plates 1 sq. cm. in area in such a way that different pressures could be applied to the oxide layer. The resistance between the brass plate in contact with the oxide and the metal base of the electrode was then measured on a post-office box.

3. Results.

3. 1. The Discharge of the Zinc, Lead Dioxide Cell; Lead Dioxide Electrode Type I.

The cell in electrolytes A, B and C at 18° and −18° C., was discharged through 8, 32 and 122 ohms. In all cases the apparent area of the oxide

and zinc electrode was 5 sq. cm.; although the area of the zinc electrode was found to be immaterial at ordinary temperature. 30 cc. of electrolyte were used in each case, the solution being renewed each time. The inter-electrode distance in the cell was the same in each case, 7·5 mm., and the size and shape of the beaker in which the electrolyte was placed was always the same.

The results are shown in graphical form in Fig. 1 and 2, while some

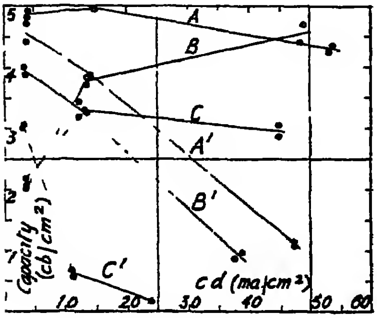
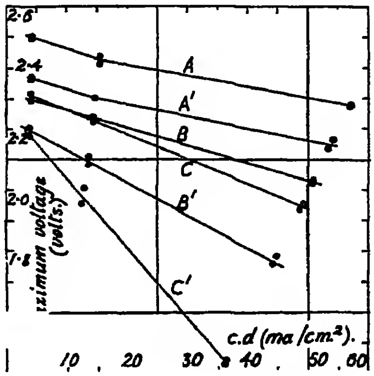


FIG. 1.



discharge curves are shown in Fig. 3. In Fig. 1, capacity is plotted against the mean c.d., and in Fig. 2 maximum voltage against maximum c.d. In both figures, graphs A, B, C are for electrolytes A, B and C respectively at 18° c. and graphs A′, B′, C′ for the same electrolytes at −18° c. In Fig. 3, in which cell voltage is plotted against time, curves A, B and C

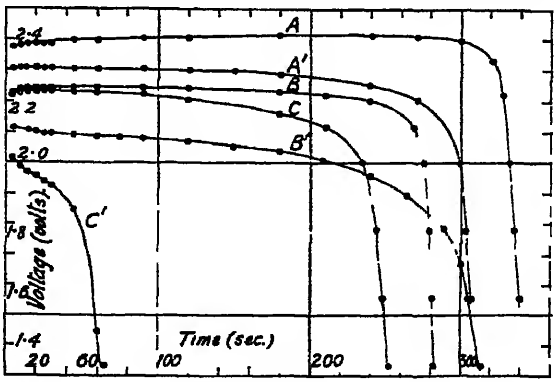


FIG. 3.

are for electrolytes A, B and C at 18° c., the external resistance being 32 ohms; curves A′, B′ and C′ for electrolytes A, B, C at −18° c., the external resistance being again 32 ohms.

3. 2. The Discharge of the Zinc, Lead Dioxide Cell, Lead Dioxide Electrolyte Type II.

The cell in normal sulphuric acid at 18° c. was discharged through 1040, 1550, 1990, 2400. 3400, 4180, 6350, 6810, 7620, 8750, 10,940, 13,100, 14,740, 20,000 and 25,000 ohms. For values of the resistance much less

than 1000 ohms, the capacity of the cell was virtually zero. In all cases, the apparent area of the zinc and oxide electrodes was 2 sq. cm., and the inter-electrode distance was 7·5 mm. The results are shown in graphical form in Fig. 4 in which capacity is plotted against the mean c.d. The maximum voltage was in all cases 2·4 v.

4. Discussion.

Fig. 1 shows that the capacity of the cell in electrolyte A is little affected by the rate of discharge within the range examined, at 18° c., though there is probably a slight fall at the highest c.d. (54 ma./cm.²). There are, however, two features of the results obtained with electrolytes B and C which may seem peculiar. These are (1) the rise in capacity with increasing c.d. at 18° c. shown with electrolyte B over the whole range, and with electrolyte C over the first part of the range; and (2) the increase of capacity at −18° c. at the lowest c.d. as compared with that at 18° c. at the same c.d. These effects are due to the chemical reaction occurring in these electrolytes between the lead dioxide and the hydrochloric acid which causes a loss of capacity. If it is assumed that at a given temperature the reaction proceeds at a constant rate, then the reaction may be represented as an addition i_2 to the actual c.d., i_1. If the life of the

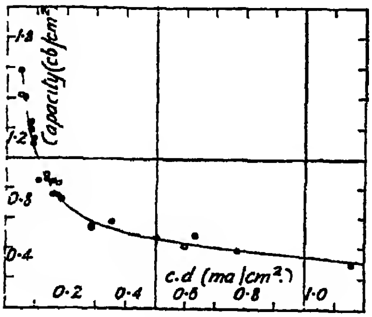


FIG. 4.

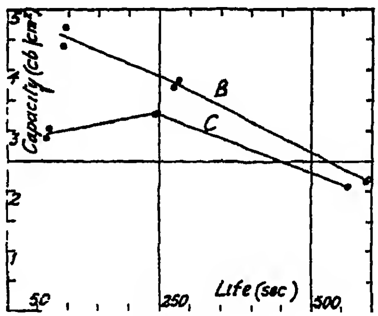


FIG 5.

cell at the c.d., i_1, is t sec., then the apparent capacity C of the oxide electrode, and therefore of the cell, is given by the equation

$$C = C_0 - i_2 t,$$

where C_0 is the true capacity of the electrode. This shows that if C is plotted against t, the life of the cell, a straight line with negative slope should be obtained. This has been done for acids B and C at 18° c. in Fig. 5. For acid B, the graph is seen to be approximately linear, and has a negative slope as required. For acid C on the other hand, though in the region corresponding to low c.d. and therefore long life, the graph appears to have a negative slope as required, it is not rectilinear. At the smallest value of t, corresponding to the highest c.d., there appears to be some additional effect causing a loss of capacity, since, from the appearance of the oxide electrode after discharge, there was no doubt that the chemical reaction occurred to a steadily smaller extent the higher the c.d. Since the chemical reaction might be expected to proceed more slowly at − 18° c., the apparent gain of capacity at the lowest c.d. at the temperature as compared with the capacity at 18° c., is explained.

Fig. 1 shows that at −18° c., the capacity is in no case independent of the c.d., but decreases with increasing c.d. The effect is greatest with

electrolyte C and least with electrolyte A. It would appear therefore that the additional effect noted only with electrolyte C at 18° c., operates in all cases at −18° c.

From Fig. 4 it can be seen that the effect of c.d. on the capacity of cells in which the lead dioxide electrode was of type II is already very large at 18° c. In addition, the c.d.'s at which the effect is observed are considerably smaller than those for the electrode of type I, even at −18° c. The reason for this may be found in the marked difference in physical form of the oxide deposit on the two electrodes. We have already noted that the deposit on type I electrodes was powdery, and very finely divided, whereas in type II it was very compact and almost metallic in appearance. It is certain, therefore, that for the same apparent area, the actual accessible area in type I is very much greater than that in type II. In view of this the conclusion seems plausible that the results found with type II electrodes correspond in fact to those obtained with type I under apparently much more severe conditions of c.d. and temperature. The similarity in form of the graph C′ in Fig. 1 and the curve in Fig. 4 supports this suggestion.

There are two points of interest in the maximum voltage graphs shown in Fig. 2. The first of these is the nonlinearity of the graphs for electrolyte A. The dependence of maximum voltage on maximum c.d. should be given by the equation

$$V = E - ir,$$

where V = the maximum voltage, E = the E.M.F. of the cell, i = c.d., and r = the internal resistance per sq. cm. of the cell. The graph of V against i should therefore be a straight line of slope $-r$. With electrolyte A, however, the slope appears to decrease with increasing c.d. It is possible that this effect has a simple explanation. In the zinc-lead dioxide cell there is a contribution to the internal resistance of the cell from the resistance between the lead dioxide and the underlying metal of the electrode. From measurements of the resistance of the dry lead dioxide electrode, there is evidence that this component of the internal resistance of the cell decreases as the current increases. In carrying out these measurements it was found that for any given pressure applied to the layer of oxide, the resistance of the electrode cdepended on the multiplying ratio on the post-office box, but was always the same for a given value of this ratio. This effect could only be due to the alteration of the current passing through the electrode when the multiplying ratio was altered. The magnitude of the current for each value of the multiplying ratio was therefore calculated and the results are shown in Fig. 6, in which the resistance per sq. cm. of the electrode is plotted against c.d. in ma./cm.². Graphs A, B, C, D correspond to pressures of 1000, 2000, 3000 and 4000 g./cm.² applied to the layer of oxide. It can be seen that in all cases the resistance decreases with increasing current. This might therefore account for the non-linearity of the graphs for electrolyte A. The linearity of the graphs with electrolytes B and C may only be apparent, since there are insufficient experimental points on the graph to enable a definite conclusion as to the form of the graphs to be made.

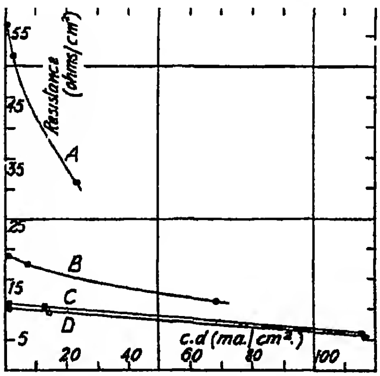


Fig. 6.

The second point of interest is the effect of temperature on the slopes of the graphs. Whereas with electrolyte A, the slope is only slightly greater at −18° c., with electrolyte B it is almost doubled, and with electrolyte C,

tripled. It is unlikely that the temperature coefficients of resistance of the lead dioxide or of the electrolytes are sufficiently large to account for such large changes in the slope. On the other hand, it was found that the effect of c.d. on capacity was greatest in electrolyte C, and least in electrolyte A. It is not unreasonable to suppose that the two effects are connected and may be attributed to a common cause.

A suggestion as to the nature of this common cause can be made from an examination of the discharge curves shown in Fig. 3. It will be seen that these are of two types. In the first, illustrated by curves A and B, the voltage diminishes only very slowly for by far the greatest portion of the life of the cell, and just before the sharp cut-off at the end of discharge, the voltage is still only slightly less than its maximum value. This type of curve was typical of cells which showed no loss of capacity other than that due to chemical reaction. In the second type of curve, illustrated by curves A^1, B^1, C^1 and possibly C, the length of the flat portion of the curve is much smaller, or non-existent, and the voltage diminishes at an appreciable rate for the greater part or the whole of the life of the cell. This behaviour was characteristic of cells which showed a loss of capacity not due to chemical reaction at the oxide electrode. Reference to Fig. 1, in which the points on the graphs at c.d.'s in the region 10-14 ma./sq. cm. correspond to the curves in Fig. 3, shows that the greater the loss of capacity, the greater the rate of decay of the cell voltage.

The form of the second type of curve is compatible with the assumption that the internal resistance of the cell increases during discharge. If the rate of increase of the resistance is sufficiently great, so that an appreciable resistance is developed in the short time (less than 0·1 sec.) required for the cell to activate after bringing the electrodes into contact with the electrolyte, the normal maximum voltage of the cell will not be reached. This could account for the abnormally large slopes of the maximum voltage graphs for electrolytes B and C at $-18°$ C.

If it is postulated that the resistance of the cell increases with the amount of electricity given by it, then it is also possible to account for a loss of capacity in the following manner. The voltage of a cell of E.M.F. E, and internal resistance r, discharging through a resistance R, is given by the relation $V = ER/R + r$; then if r increases sufficiently, the cell may appear to collapse before it has been completely discharged. The capacity of the cell would therefore appear to be less than normal under these conditions. The effect of c.d. on the capacity may also be predicted. The above expression for the voltage of the cell may be rewritten as

$$\frac{1}{V} = \frac{1}{E}\left(1 + \frac{r}{R}\right)$$

let $\Delta(1/V)$ be the change in $1/V$ corresponding to the change in cell voltage from its initial value, which may be taken as the maximum value, to the value at the end of discharge.

The change in r required to produce this change $\Delta(1/V)$ is therefore given by the equation

$$\Delta\left(\frac{1}{V}\right) = \frac{1}{E}\left(1 + \frac{\Delta r}{R}\right)$$

where $\Delta r =$ the change in r. In the present instance, as shown by the curves in Fig. 3, the discharge could be regarded as complete when the cell voltage had fallen to 75 % of its maximum value. $\Delta(1/V)$ is therefore equal to $1/3V^m$ where V^m is the maximum voltage. For a given value R of the external resistance

$$\frac{1}{3V^m} = \frac{1}{E}\left(1 + \frac{\Delta r}{R}\right) \quad \therefore \Delta r = R\left(\frac{E}{3V^m} - 1\right).$$

If 2 different values of the external resistance, R_1 and R_2 are employed, we shall then have

$$\frac{\Delta r_1}{\Delta r_2} = \frac{R_1}{R_2}\left(\frac{\frac{E}{3V_1^m} - 1}{\frac{E}{3V_2^m} - 1}\right.$$

The expression in brackets may be taken as unity to a first approximation since the change in V^m due to a change in R, the external resistance, is small compared with the change in R itself. (Even in the case of electrolyte C at $-18°$ c., the maximum voltage of the cell, is less than halved when R, the external resistance, is reduced 15 times from 122 ohms to 8 ohms.)

To a first approximation, therefore,

$$\frac{\Delta r_1}{\Delta r_2} = \frac{R_1}{R_2}$$

so that if $R_1 > R_2$, $\Delta r_1 > \Delta r_2$. Thus, the greater R, that is, the smaller the rate of discharge, the greater Δr must be to cause premature collapse of the cell. Since it has been postulated that the internal resistance of the cell increases with the amount of electricity passed, then a greater value of Δr corresponds to a greater amount of electricity passed. The capacity of the cell will therefore appear to increase as the c.d. is lowered. If the c.d. is sufficiently reduced the cell may give its full capacity before r reaches a value sufficient to cause premature collapse of the cell. Under these conditions the capacity would be independent of c.d. These predictions are in qualitative agreement with the results.

A physical explanation of the increase of internal resistance during discharge of the cell may be found in the coating of the particles of lead dioxide with a protective film of some substance formed in the course of discharge. In sulphuric acid, such a substance might be lead sulphate, or in phosphoric acid, lead phosphate. In this connection the interesting observation was made that when the zinc-lead dioxide cell in which the oxide electrode was of type II, was discharged in an electrolyte such as perchloric acid, nitric acid, or trichloracetic acid in which no insoluble lead salt is formed in the cell reactions, the capacity was much more normal at the normal c.d.'s of 4-30 ma./cm.^{2}. In trichloracetic acid in fact the capacity was virtually equal to the theoretical capacity of the oxide electrode. With the electrode of type II, in sulphuric acid, owing to the much smaller actual area of exposed surface of lead dioxide, the amount of electricity which must be passed to give the same protection under the same conditions would be expected to be considerably less than in the case of the electrode of type I where the actual area is considerably greater. This would account for the different results obtained with the two types of electrode.

This work was carried out under an extra-mural research contract of the Ministry of Supply and the authors are indebted to the Chief Scientist of the Ministry for permission to publish.

5. Summary.

The capacity of the zinc-lead dioxide cell has been found to depend on the nature of the oxide-electrode, the nature of the electrolyte, its temperature, and the rate of discharge.

It is suggested that this is due to protection of the oxide electrode by substances formed in the course of discharge of the cell.

Résumé.

On a trouvé que la capacité de la pile Zn-bioxyde de Pb dépend de la nature de l'électrode de bioxyde, de la nature de l'électrolyte, de la tem-

pérature de celui-ci et de la vitesse de décharge. Ceci est probablement dû à la protection de l'électrode de bioxyde par des substances formées pendant la décharge de la pile.

Zusammenfassung.

Es wurde gefunden, dass die Kapazität des ZinkBleidioxydelements von der Art der Herstellung der Oxydelektrode, der Temperatur und der Entladungsgeschwindigkeit abhängt. Es wird vorgeschlagen, dass dies auf einen Schutzüberzug der Oxydelektrode, der aus während der Entladung gebildeten Substanzen besteht, zurückzuführen ist.

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THE POTENTIAL OF ION-EXCHANGING SUBSTANCES.

BY H. J. C. TENDELOO.

Received 10*th February*, 1947.

The knowledge of the *p*H is of great importance in understanding a number of processes, both in chemistry and biology; its measurement can be done easily, quickly and with accuracy. It would be of great value to have similar methods available for the determination of the activity of sodium, potassium, calcium and magnesium, because these ions are also important in biology and e.g. in soil science; consequently researches have been conducted during several years to find suitable electrodes. Though the activity of the ions just mentioned may be determined using an amalgam of the elements, these electrodes have only limited significance on account of the interference of other ions. Moreover, the methods are difficult.

Therefore other methods have been investigated. Thin plates of mineral CaF_2, sealed on a glass tube—filled with a solution of $CaCl_2$ and provided with an Ag-AgCl electrode—were used as calcium electrodes, but the reproducibility of the electrodes was bad, and their usefulness in mixtures of electrolytes was very limited.

Electrodes were prepared by placing muscovite for several days in weak alkaline solutions of sodium, potassium or calcium ions, so as to replace the exchangeable ions of the surface of the muscovite electrodes by sodium, potassium or calcium, thereby allowing the surface to function as an electrode for one of these ions. However, after some measurements in dilute solutions, $c = 10^{-3}$ to 10^{-4} M., the electrode had lost its special function and had become a hydrogen electrode because hydrogen ions had replaced the metal ions on the surface.

Marshall investigated membranes of bentonite,[1] beidellite [2] and other minerals for use as potassium, sodium and calcium electrodes.

The following is a survey of investigations in collaboration with A. J. Zwart Voorspuij and G. J. Vervelde.

The Glass Electrode.—It is known [3] that the glass composition is of primary importance and McInnes and Dole were the first to show that

[1] Marshall and Bergman, *J. Amer. Chem. Soc.*, 1941, 63, 1911.

[2] Marshall and Krinbill, *ibid.*, 1942, 64, 1814.

[3] A survey of the older literature may be found in *Ann. Reports*, 1934, 30, 285; Zwart Voorspuij, *Diss.* (Utrecht, 1943); Tendeloo and Zwart Voorspuij, *Rec. trav. chim.*, 1943, 62, 784, 793.

different glass compositions have their own characteristics when used as hydrogen electrodes. Corning glass 015 is to be preferred, but it is unsuitable when the p_H is higher than about 9, or lower than about 2. Horovitz suggested that adsorption plays an important role in establishing the potential of the glass electrodes. Lengyel and Blum found that special properties appeared when a glass contained Al_2O_3 or B_2O_3, whereas substitution of sodium in the glass by potassium, lithium or calcium did not materially influence the behaviour towards hydrogen ions.

When a glass electrode behaves as an ideal hydrogen electrode, its value is 57·7 mv. at 18° C. for $\Delta p_H = 1$. If, however, other ions take part in establishing the potential this value decreases. It is clear that all ions present in a solution will interfere with the surface's ability to exchange its ions with those in the solution. Numerous researches on soils, permutites, minerals, clays, etc., prove that ion exchange, as first mentioned by Way,[4] takes place and that this is of great importance for fertility, soil structure, etc. Researches on other ionogenic surfaces, e.g. cellulose, starch, proteins, gum arabic, also point to ion-exchange. The fact that Corning glass 015 is rather insensitive to other ions, except those of hydrogen, providing their concentrations are not too high, must have something to do with its physico-chemical properties.

It is of interest to note that minerals containing aluminium ions with the co-ordination value of four show cation exchange, according to van der Meulen.[5] In the light of the work of Lengyel and Blum, a glass containing Al_2O_3 was investigated in solutions of different salts, the p_H varied, in an attempt to find a theoretical explanation for this.

It was decided to use a glass containing 6 % CaO, 14 % Li_2O, 10 % Al_2O_3 and 70 % SiO_2 by weight. The glass was blown out and a thin glass membrane was sealed on to one end of a glass tube. A solution of hydrogen chloride with quinhydrone and a Pt-electrode allowed connection with the potentiometer. The cell was completed in the ordinary way, using a saturated calomel electrode.

The description of the experimental method, together with the results and a mathematical treatment of the potential of the glass electrode, may be omitted here as it has been published elsewhere.[6]

The theory is based principally on the adsorption formula of Langmuir, written as

$$[HX] = \frac{K'_1 \, . \, A \, . \, [H^+]}{1 + K'_1[H^+]} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A is the number of adsorption centres per unit surface, of which a number is saturated by adsorbed H-ions, [HX], and the rest is present as $[X^-]$, so that

$$A = [X^-] + [HX]. \quad . \quad . \quad . \quad . \quad (2)$$

Assuming the glass to be a weak acid with a dissociation constant K_1

$$K_1 = \frac{[H^+][X^-]}{[HX]} \quad . \quad . \quad . \quad . \quad (3)$$

where K'_1 is given by :

$$K'_1 = \frac{1}{K_1}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Applying the same considerations to other equilibria when sodium and calcium ions are present in the solution, viz.

$$K_2 = \frac{[Na^+][X^-]}{[NaX]} \quad . \quad (5) \qquad K'_2 = \frac{1}{K_2} \quad . \quad . \quad (6)$$

$$K_3 = \frac{[Ca^{++}]^{\frac{1}{2}} \, . \, [X^-]}{[Ca_{\frac{1}{2}}X]} \quad (7) \qquad K_3' = \frac{1}{K_3} \quad . \quad . \quad (8)$$

[4] Way, *J. Roy. Soc. Eng.*, 1850, **11**, 313 ; 1852, **13**, 123 ; 1854, **15**, 491.
[5] van der Meulen, *Rec. trav. chim.*, 1935, **54**, 107.
[6] Cf. [3].

and substituting in the Nernst formula for the potential of a hydrogen electrode:

$$E = \frac{RT}{F} \ln \frac{c_H}{C_H} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where c_H equals the hydrogen ion concentration in the solution and C_H equals the concentration of the adsorbed hydrogen ions on the glass membrane, i.e. [HX] one obtains

$$E_g = \frac{RT}{F} \ln (1 + K'_1[H^+] + K'_2[Na^+] + K'_3[Ca]^{\frac{1}{2}}) + C_1 \quad . \quad (10)$$

or, in general, for different ions A, B, C . . . with valencies a, b, c . . .

$$E_g = \frac{RT}{F} \ln (1 + K'_1[A^+]^{1/a} + K'_2[B^+]^{1/b} + K'_3[C^+]^{1/c} + \ldots) + C. \quad (11)$$

Considering the deviation of the glass electrode from its behaviour as an ideal hydrogen electrode, E_H,

$$E_H = \frac{RT}{F} \ln [H^+] + C_2 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

it follows from (10) and (12)

$$E_g - E_H = \Delta E' = \frac{RT}{F} \ln \left(1 + \frac{1}{K'_1[H^+]} + \frac{K'_2[Na^+]}{K'_1[H^+]} + \frac{K'_3[Ca^{++}]^{\frac{1}{2}}}{K'_1[H^+]}\right) + C_3 \quad (13)$$

The curve obtained by plotting $\Delta E'$ against the pH will deviate from the straight line parallel to the pH-axis as soon as the glass electrode is no longer an ideal hydrogen electrode. Writing (13)

$$\Delta E' = \Delta E + C_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

then ΔE may be calculated from the measurements.

Restricting the considerations to H-ions and Na-ions one may easily deduce that

$$e^{\frac{F\Delta E}{RT}} - 1 = \frac{1 + K'_2[Na^+]}{K'_1} \cdot \frac{1}{[H^+]} \quad . \quad . \quad (15)$$

$$\log (e^{\frac{F\Delta E}{RT}} - 1) = D = \log B + pH, \quad . \quad . \quad . \quad (16)$$

where
$$B = \frac{1 + K'_2[Na^+]}{K'_1}.$$

Plotting D against pH, one can calculate log B and therefore obtain a value of $K_1 = \frac{1}{K'_1}$, the assumed dissociation constant of the glass. It has been found that a glass containing Al_2O_3 has a greater dissociation constant than Corning glass 015.

These researches showed, as had been found earlier by other investigators, that on changing the glass composition, the glass becomes more sensitive to other ions, as compared with Corning glass 015, and that a characterisation of a glass, by something like a dissociation constant may give information about its usefulness as an electrode for different ions; it seems worth while, therefore, to continue these researches with other compositions.

Potential of Plant Roots.

The potential of plant roots has been investigated by Lundegårdh.[7] He stated that the passage of ions in and out is principally regulated by exchange processes, and that the phenomena obeys the principles of membrane equilibrium and mass action laws. The protoplasma membrane is assumed to be a layer of oriented molecules, a small number of

[7] Henrik Lundegårdh, *Arkiv. Botanik*, 1945, 32, 1.

which is dissociated, giving rise to the electric charge. Since the acidic properties prevail over the basic, the membrane substance behaves as a rather strong acid.[8] Similarly, Jenny,[9] using radioactive potassium, could prove that potassium ions could pass in and out of a root.

The curves of the potential of a root as a function of the concentration of potassium ions in the outside solution (denoted by the negative logarithm of the concentration) could be described by an extension of the theory of the Donnan equilibrium.[10]

Assuming that a plant root consists of protoplasm which exchanges ions with the surrounding medium and which behaves as a weak acid ("root-acid") with a dissociation constant K and a membrane, impermeable to this acid and its anions, but permeable to hydrogen and potassium ions, the theory may be developed as follows.

The concentration of the root-acid, HZ, being A one obtains according to mass action law

$$K = \frac{[Z^-][H^+]}{[ZH]} \qquad (17)$$

and with $[Z^-] + [ZH] = A$,

$$[Z^-] = \frac{AK}{K + [H^+]}. \qquad (18)$$

Putting $K' = \frac{1}{K}$,

$$[Z^-] = \frac{A}{1 + [H^+]K'}. \qquad (19)$$

If the root is placed in an acid solution of potassium chloride the Donnan equilibrium will be

		Root.					Membrane.	Solution.		
Components .	HZ	Z^-	K^+	H^+	Cl^-	|	K^+	H^+	Cl^-
Concentrations	$A - z_1$	z_1	y_1	y_2	z_2	|	c_1	c_2	c_1+c_2

In this equilibrium one has

$$v = \frac{c_1}{y_1} = \frac{c_2}{y_2} = \frac{z_2}{c_1 + c_2} \qquad (20)$$

and

$$z_1 + z_2 = y_1 + y_2 \qquad (21)$$

and with (19)

$$z_1 = \frac{A}{1 + K'y_2}.$$

From (20) and (21) it follows that

$$v^3 + \left(K'c_2 + \frac{A}{c_1 + c_2}\right)v^2 - v - K'c_2 = 0. \qquad (22)$$

Assuming values for A, K' and c_2 one can calculate at different values of c_1, the corresponding values of v. Now according to Nernst the potential of the root at 18° c. is

$$E = -57{\cdot}7 \log v \qquad (23)$$

which can be calculated.

The calculated curves show a great similarity with the experimental ones. Next an attempt to calculate K' and A from experimental data was made. Knowing c_1, c_2 and v one can obtain, using two measurements, the values of K' and A. Recalculating E with the values of K' and A, and comparing these calculated values with the measured ones, the results of the following tables were obtained.

[8] *Idem., Protoplasma*, 1941, **35**, 548.
[9] Jenny and Overstreet, *Proc. Nat. Acad. Sci.*, 1938, **24**, 384.
[10] Tendeloo, Vervelde and Zwart Voorspuij, *Rec. trav. chim.*, 1944, **63**, 97; *Versl. Ned. Akad. Wet.*, 1944, **53**, 169.

Table I gives the results for *Triticum vulgare* as found by Lundegårdh where c_2 was assumed to be 10^{-5}, the hydrogen-ion concentration of carbon dioxide containing solutions of neutral electrolytes. From the measurements one calculates $A = 0{\cdot}09$ and $K' = 400$.

In Table II the results on *Solanum tuberosum*, obtained in this laboratory, have been summarised; here, for $c_2 = 10^{-5}$, one calculates $A = 0{\cdot}04$ and $K' = 12000$. The experimental method has been described elsewhere and may be omitted here.[11]

TABLE I.

c_1.	$> 10^0$.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.
$E_{exp.}$		+267	+222	+180	+132	+115
$E_{cal.}$	+282	+271	+227	+175	+135	+110

Mattson [12] has already proved that the ion exchange of soils and sponges shows all the characteristics which are to be expected from the theory of the Donnan equilibrium. As a result, it may be possible to characterise soils, clays and other ion-exchanging substances, as well as plants, by the two constants appearing in the extended theory of the Donnan equilibrium as mentioned above. The same considerations may be of interest in further investigations on surface potentials, and perhaps on the electrophoresis of proteins and other colloids. Thus, the curves of surface potentials of Dervichian [13] and the curves of the electrophoresis of proteins [14] show similarities with those obtained with the theory mentioned here.

TABLE II.

c.	$> 10^0$.	10^0.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.
$E_{exp.}$		+265	+263	+240	+202	+169	+161
$E_{cal.}$	+265	+265	+261	+237	+198	+166	+143

Summary.

The potential of ion-exchanging substances has been discussed. It is shown that, depending on its composition, a glass can function nearly exclusively as an electrode for hydrogen-ions or for other ions as well, if it contains Al_2O_3. A "dissociation constant" of the glass can be calculated; this appeared to be greater for an Al_2O_3-containing glass than for Corning glass 015. A theory, based on ion-exchange and adsorption, is developed for the potential of a glass electrode, and is in accordance with experimental results.

The potential of plant roots is described by an extension of the Donnan equilibrium theory. Assuming the non-diffusible anions here to belong to a weak acid a theory is given which is in accord with the experimental results, and which allows a calculation of the dissociation constant of the acid. It may be possible to characterise different plants by (*a*) the dissociation constant and (*b*) the concentration of the weak acid in the root. The theory may also be applicable to other phenomena.

[11] cf. [10].

[12] Mattson, *Ann. Agr. Coll. Sweden*, 1942, **10**, 56; Mattson and Larsson, *ibid.*, 1944-45, **12**, 21.

[13] Dervichian, *J. Chem. Physics*, 1939, **7**, 931.

[14] Abramson, Moyer and Gorin, *Electrophoresis of Proteins* (New York, 1942.)

Résumé.

On discute ici le potentiel de corps échangeurs d'ions. Selon sa composition, un verre peut fonctionner presqu'exclusivement comme une électrode pour ions H^- ou, s'il contient Al_2O_3 par exemple, aussi pour d'autres ions. Différents verres peuvent être caractérisés par leur " constantes de dissociation " et une théorie qui s'accorde avec les résultats expérimentaux est développée.

Le potentiel des racines des plantes est expliqué par la théorie—étendue—de l'équilibre de Donnan, dans laquelle les anions non diffusables proviennent d'acides faibles dont on peut calculer la constante de dissociation. Celle-ci, en même temps que la concentration de l'acide dans la racine, est caractéristique de la plante. La théorie générale peut être appliquée à d'autres phénomènes.

Zusammenfassung.

Der Artikel erörtert das Potential von ionenaustauschenden Substanzen. Je nach seiner Zusammensetzung kann sich ein Glas entweder fast ausschliesslich als Wasserstoffionenelektrode oder, wenn es z.B. Al_2O_3 enthält, auch als Elektrode für andere Ionen verhalten. Verschiedene Gläser können durch ihre " Dissoziationskonstanten " charakterisiert werden. Es wird eine Theorie entwickelt, mit deren Hilfe die Versuchsresultate erklärt werden.

Das Potential von Pflanzenwurzeln kann durch eine Erweiterung der Donnan-Gleichgewichtstheorie erklärt werden, wobei die nichtdiffundierenden Anionen von einer schwachen Säure abstammen, deren Dissoziationskonstante berechenbar ist. Dieser Wert in Verbindung mit der Säurekonzentration in der Wurzel ist für die Pflanze charakteristisch. Die allgemeine Theorie ist möglicherweise auch auf andere Erscheinungen anwendbar.

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(a) GENERAL DISCUSSION.*

Dr. R. L. Tichenor (*West Orange, New Jersey*) (*partly communicated*): The maximum found in the voltage-charge curves of Hickling and Taylor (Plate 1, B and C, curves 2) and the subsequent decrease in voltage do not seem to be explained entirely by the authors' assumption of the formation of an unstable, higher oxide undergoing rapid decomposition. This single assumption requires a curve which rises asymptotically to the potential corresponding to the steady-state concentration of the unstable oxide and thus does not account for the observed maximum.

A possible explanation of this phenomenon may be found in the following picture of the charging mechanism. During anodic oxidation, the silver surface is first covered uniformly with Ag_2O to a depth of about three molecules. The formation of trivalent silver then begins accompanied by a rise in potential and an increase in the oxygen content of the oxide layer. This increase in oxygen content might be expected to lead to an increased volume of the film but, since it is attached to the silver substrate, the first result is the creation of compressive forces which soon are strong enough to cause the surface layer to crack or crumple; it is at this point that the potential reaches its highest value and begins to decline. From here on various portions of the surface undergo these

* On eight preceding papers.

processes at different times; at any one moment some parts are freshly uncovered metal while other regions contain various concentrations of trivalent silver under different compressive forces.

This mechanism can account for the observed temperature and time effects of Plate I B and C if it is assumed that increased temperature aids the crumpling of the oxide layer and that the probability of crumpling increases with the time the compressed layer has existed.

Dr. A. Hickling (*Liverpool*) said: With reference to Tichenor's comment on the oscillograms for silver, I think his argument is quite sound and I am indebted to him for drawing our attention to this point which we had not previously considered in detail. The probable explanation is, I think, that the decomposition of the unstable silver peroxide is autocatalytic which would, of course, account for the peak in the oscillograms.

Dr. M. Haissinsky (*Paris*) said: The potentials measured by the authors for the $Ag—Ag_2O$ electrode in the 3 solutions of different *p*H, viz., NaOH (*p*H about 14; potential, 0·40 v.), Na_2CO_3 (*p*H 12·; 0·52 v.) and $Na_2B_4O_7$ (*p*H 9·2; 0·67 v.) are in good agreement with the theoretical equation:

$$E = E_0 + 0{\cdot}058 \log (OH^-)$$

corresponding to the reaction:

$$2Ag - 2OH^- = Ag_2O + H_2O + 2e.$$

It is easy to see that the same dependance of *p*H (with, of course, another E_0) must hold for the higher silver oxide whatever its composition may be, provided it is insoluble. It would be interesting to verify this experimentally. Kolthoft found,[1] indeed, a very important deviation from the thermodynamic equation in the case of lead dioxide and I found a similar result for the nickel peroxide.[2] In both the cases it is difficult to find a simple mechanism to explain these observations.

Dr. H. Wilman (*London*) said: The abnormality of a maximum of overpotential in Plates 1B and 1C of the paper by Dr. Hickling and Dr. Taylor has been referred to by Dr. Tichenor. In this case again the stepwise rise in the overvoltage suggests a compound formation, which may be Ag_2O_3 at the higher potential stage. Some observations I made, during the early part of the war, on oxidation of silver by various methods in connection with photoelectric cells, may give a possible explanation of the decomposition stage which Dr. Hickling associates with the final decline in potential. I found that some samples of Ag_2O_3, which I had freshly prepared and examined by electron diffraction on thin collodion films, did give complicated patterns of spotty rings obviously not due to Ag or Ag_2O, but the crystal structure was not determined. Several samples, however, appeared to have decomposed, giving patterns entirely due to normal silver, but showing that the silver crystals were in the form of large, but extremely thin, flake-like layers parallel to the octahedral (111) planes, which were also parallel to the collodion substrate. If the oxidation of Ag to Ag_2O_3 is a reversible reaction, as Dr. Hickling suggests, it may be that when the concentration of Ag_2O_3 has reached a high enough value the decomposition part of the reaction may lead to formation of Ag crystals in this form, so that the smooth exposed (111) faces of these, containing the closest possible packing of Ag atoms, would be relatively more difficult to reoxidise as I have already described, and hence the reaction would set in more and more towards a decomposition, with a corresponding fall in the potential.

Dr. T. P. Hoar (*Cambridge*) (*communicated*): The behaviour of iron anodes in alkaline chloride solutions is of great interest. I believe that the "activating" influence of chloride ions may be best explained, not by a selective adsorption of Cl^- as postulated by Kabanov, nor by the conception of a high "penetrating power" of Cl^- for oxide films as argued

[1] Quoted by Kolthoff and Furman, *Potentiometric titrations* (New York, 1931).
[2] Haissinsky and Quesney, *Compt. rend.*, 1947, **234**, 831.

by Britton and Evans,[3] but by a consideration of the influence of a non-depositing ion such as Cl^- on the *p*H of the electrolyte next to the anode.

When only OH^- ions are present, solid $Fe(OH)_2$ is produced, repairing the passivating film on the anode; the electrolyte at the anode is constantly replenished by migrating OH^-, and can never become acid. But when Cl^- ions are also present, part of the current is carried by them, and since the anodic product in alkaline chloride solution is still $Fe(OH)_2$, the concentration of Cl^- at the anode rises rapidly, while that of OH^- falls. Even when the OH^- concentration at the anode has fallen to very low values corresponding to *p*H values below 7, solid $Fe(OH)_2$ is still formed, owing to the smallness of the ionic product $(Fe^{++})(OH^-)^2$; but eventually the anolyte becomes so acid that substantial concentrations of dissolved ferrous iron can exist in it, and at this point "breakdown" of the oxide film, due to undermining by the conversion of solid metal to *liquid* products, occurs. Subsequent precipitation of Fe^{++} by the OH^- in the *bulk* of the solution results in non-adherent, non-passivating material.

The above mechanism accounts for the initial rise in potential at an iron anode in alkaline chloride solution (film repair by solid $Fe(OH)_2$) followed by a fall (film undermining due to formation of soluble products), as illustrated in Fig. 6 of Kabanov's paper. Analogous effects have been found at tin anodes,[4] and on naturally corroding tin [4, 5] and iron,[6, 7] where the oxide film provides a local cathode for its anodic pores. The mechanism also gives a clear picture of why the rate of the anodic reaction of iron in alkaline chloride solutions is the same as that in acid solutions at the same potential, as shown by them; for the electrolyte next to the iron anode rapidly becomes acid, and is maintained so owing to the transport of Cl^- to the anode and to the small ionic product of $Fe(OH)_2$. I entirely agree with these authors that "the Cl^- ion allows Fe^{++} to be formed, but does not participate in the process itself" and that "Cl^- ion . . . hinders the passivation of iron", but I think that the above explanation in terms of transport and solubility gives a better picture of the situation than the Cl^- adsorption hypothesis. Further support for the mechanism is given by experiments on the influence of the ClO_4^- ion on film breakdown, shortly to be published; I find that ClO_4^- is as potent as Cl^-, as would be expected on the transport-solubility theory, but not on an adsorption theory, since ClO_4^- is particularly non-deformable and would not be expected to be readily adsorbed.

In solutions initially containing a very high OH^-/Cl^- ratio, of course, film repair by $Fe(OH)_2$ becomes complete before OH^- is exhausted at the points where iron is reacting, and no breakdown can ever occur.

Prof. H. J. C. Tendeloo (*Wageningen*) said: In addition to the results described in the paper, further results on *Sinapis alba*, might be mentioned; these are tabulated in Table III.

TABLE III.

Conc. KCl c_1	2×10^{-1}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
Number of observations	5	30	30	30	30	30
Mean value E	+16·0	+12·47	−7·87	−29·37	−44·27	−51·43
Γ calculated	—	0·802	0·356	0·151	0·0832	0·0627

[3] Britton and Evans, *J. Chem. Soc.*, 1930, 1780.
[4] Brennert, *Tech. Pub. Int. Tin Res. Dev. Council*, No. 2, 1935.
[5] Hoar, *Trans. Faraday Soc.*, 1937, 33, 1152.
[6] Lochte and Paul, *Trans. Electrochem. Soc.*, 1933, 64, 23.
[7] Hoar (unpublished work).

According to

$$K'C_2 + A\frac{V^2}{(V^2 - 1)(c_1 + c_2)} = -V \quad . \quad . \quad . \quad (23)$$

which can easily be derived from (22), there must be a linear relationship between

$$\frac{V^2}{(V^2 - 1)(c_1 + c_2)} \text{ and } -V,$$

K', c_2, and A being constant.

Whether this relationship is correct depends on the value of c_2, the hydrogen ion concentration in the immediate surrounding of the root, which cannot be determined. Calculating for different values of c_2 the linear relationship is best obtained for

$$c_2 = 3 \cdot 2 \times 10^{-4}$$

as can be seen from the Fig. 1.

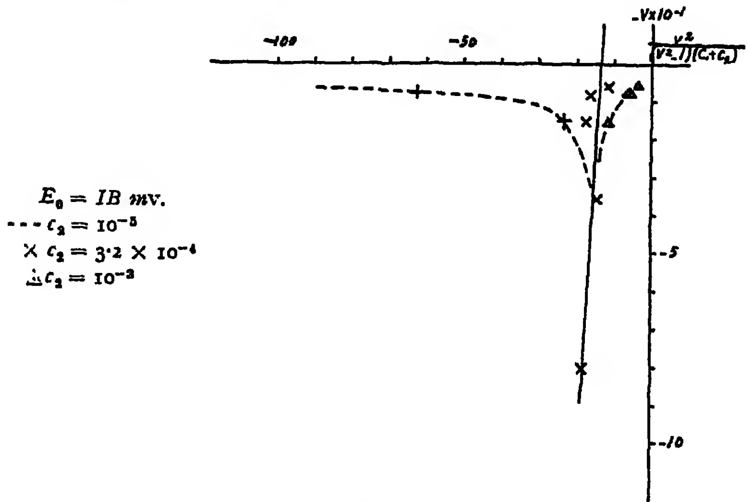

FIG. 1.

Using (23) and calculating the values of K' and A, one gets

$$K'c_2 = 0 \cdot 754 \quad c_2 = 3 \cdot 2 \times 10^{-4}$$
$$K' = 2 \cdot 36 \times 10^3 \quad A = 0 \cdot 0653.$$

Using these values in

$$V^3 + \left(K'c_2 + \frac{A}{c_1 + c_2}\right)V^2 - V - K'c_2 = 0,$$

to calculate V, and accordingly E, and comparing $E_{calc.}$ and $E_{exp.}$ one gets the results of Table IV.

TABLE IV

Conc. KCl c_1	$>10^0$	2×10^{-1}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
E exp. . .	—	+16·0	+12·47	−7·87	−29·37	−44·27	−51·43
E calc. .	+18·0	+15·8	+13·7	−5·7	−32·6	−47·7	−51·0

In conclusion one may state again that a root can be characterised by two constants. The measurements have been done by W. H. v.d. Molen.

Dr. P. Gross (*Slough*) said: A model for the glass electrode very similar to the one presented here was proposed many years ago.[8] The essential difference was that a distribution, and not an adsorption, equilibrium between glass and solution was considered. This led to a formula for the deviations from the ideal hydrogen electrode,[9] which seems very similar to Dr. Tendeloo's formula, and which represented the then best experimental data quite well. The two formulæ ought to become identical at low sorption values. It would be of interest to know if this is really the case, and also if the two formulæ can be distinguished experimentally.

Prof. D. H. J. Tendeloo (*Wageninen*) said: Mr. D. C. Henry said that he measured the *p*H of bentonite suspensions with ordinary glass-electrodes. The potential was not constant but showed a drift, which was not a consequence of the well-known suspension effect. After having filtered off the suspended particles the drift was found again in the clear liquid. As there seems to be a small solubility of bentonite, the drift of the electrode potential may be in accordance with the results obtained with glass-electrodes containing Al_2O_3, for any dissolved bentonite produces aluminium silicates which will influence the surface of an ordinary glass-electrode. I agree with Mr. Henry's explanation: research is now going on with other glass compositions, containing lesser amounts of Al_2O_3 as mentioned before.

The equation of Gross and Halpern, although showing great similarity, is not the same as eqn. (10) and (11) of my paper.

[8] Gross and Halpern, *Z. physik. Chem.*, 1925, **115**, 54, 1925, **118**, 255.
[9] Gross and Halpern, *J. Chem. Physics*, 1934, **2**, 137.

SOME INVESTIGATIONS ON THE OXYGEN—OVERPOTENTIAL IN MOLTEN SALTS.

By H. Flood and T. Førland.

Received 10*th February*, 1947.

The overpotential at an electrode is defined as the potential difference between this electrode and a similar unpolarised electrode in the same solution.

In an earlier investigation Karpatscheff and Patzug [1] measured the oxygen overpotential at platinum in molten mixtures of KNO_3, $NaNO_3$ and $LiNO_3$ at temperatures between 150°-250° C. They found the overpotential to be of an activated type. Agar and Bowden [2] examined the oxygen overpotential on platinum and nickel, in molten NaOH at 350° C. and found a typical concentration overpotential which depended on the increase in H_2O concentration in the immediate vicinity of the electrode. With a small excess of Na_2O the overpotential was determined by the decrease of Na_2O in the vicinity of the electrode.

The present investigations were carried out in order to study the possibility of using the oxygen electrode in measurements of oxygen ion activities. The systems investigated, therefore, contained ordinary buffers, of the type:

$$\text{Base} = \text{Acid} + O^{--} (PO_4^{---} = PO_3^- + O^{--})$$

(cp. H. Lux [3, 4]).

[1] Karpatscheff and Patzug, *Z. physik. Chem.*, 1935, **173**, 383.
[2] Agar and Bowden, *Proc. Roy. Soc. A.*, 1939, **169**, 206.
[3] Lux, *Z. anorg. allgem. Chem.*, 1942, **250**, 159.
[4] Lux, *Z. Elektrochem.*, 1939, **45**, 303.

Experimental.

The experimental method was in general the same as that used by Agar and Bowden. The anode was a platinum sheet of 1 cm.^{2} and a platinum wire placed near the anode served as reference electrode. Pure, dry oxygen was continuously bubbled through the melt when the cell was in operation. The melt was contained in a platinum crucible, which also served as cathode. The overpotential generally needed a long time to reach a constant value, e.g. about 15 min. at 700° c. The measurements were not very reproducible, but the general character of a potential curve from a single run of observations was always the same. It is remarkable that in the phosphate and sulphate melts at high c.d.'s a sudden jump (of about 0·3 v.) in the potential could sometimes be observed. The results are given in Table I. It was not possible to find any relation between the overpotential and the acidity (cp. the variation of $N_{PO_4^{---}}/N_{PO_3^-}$ in system V) of the melt.

Discussion.

The overpotential phenomena in pure Li-Na sulphate, and in sulphate, phosphate, silicate and carbonate solution in Li-Na fluoride showed a

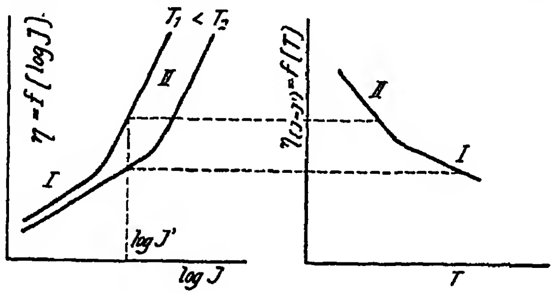

FIG. 1.

remarkably similar character. By plotting $\eta = f$ (log I) we find that the curves of these systems have two different sections (I and II, cp. Fig. 1). In section I the slope has a value of the order $RT/3F$; in the section II, on the contrary, the slope is about RT/F.

By increasing the temperature the transition interval between the two sections is moved towards higher current densities. In the two sections there is a distinct difference in the temperature coefficient of the overpotential. By examining the overpotential as a function of the temperature, a dependence as shown in Fig. 1 was found.

At low temperatures the slope is linear with a value $d\eta/dT = -1{\cdot}5$ mv./°c. This is the temperature coefficient corresponding to section II. On increasing the temperature a change of direction of the curve is observed. The slope is again linear, but now with a lower value corresponding to $d\eta/dT = -0{\cdot}4$ mv./°c. This corresponds to the temperature coefficient in the section I.

Section I, which occurs at low c.d. and high temperature, shows a low temperature coefficient of the overpotential. It is therefore probably of the concentration overpotential type.

In section II, which occurs at low temperature and high c.d., the value of the temperature-coefficient is distinctly higher. Here an activated electrode process is supposed to be rate-determining. In fluoride melts, the overpotential decreases in the following order:

$$SO_4^{--} > PO_4^{---} > CO_3^{--} > SiO_4^{----}.$$

TABLE I

	System.	$\eta = b \log I/I \pm \Delta$.					Temperature Coeff.			Alteration o η for 50 % Decrease in the Oxygen Flow.		Remarks.
		Temp. °c.	b Volt.	I_0 ma./cm.²	Δ Volt.	I ma./cm.²	$d\eta/dT$. mv./°c.	I ma./cm.²	Temp. °c.	Alteration %	I ma./cm.²	
I	Li_2SO_4, Na_2SO_4 (2 : 3)	700	0·20	0·022	0·02	0·05-2	— 1·5 — 0·3	0·5 0·5	700-890 950-1000			Addition of 10 mol. % NaF gave only a small alteration in overpotential.
II	„	900	0·06 0·21	0·015 0·1	0·006 0·01	0·05-0·15 0·5-5						
III	1·25 mol. % Na_2SO_4 in NaF, LiF (2 : 3)	700	0·07 η =	0·01 0·42	0·01 0·03	0·05-1 5-40						
IV	1·25 mol. % Na_3PO_4	700	0·06 0·18	0·01 0·63	0·015 0·03	0·05-1 10-80	— 0·4 — 0·4 — 1·2 — 0·4	0·5 10 40 40	650-750 650-750 700-800 800-900	6 8	0·5 10	
	1·25 mol. % $NaPO_3$ in NaF, LiF (2 : 3)		0·22	0·023	0·015	— 0·25-— 0·05	— 3·1	— 0·1	650-750	2	— 0·1	
V	1·25 mol. % Na_3PO_4 0-2 mol. % $NaPO_3$ in NaF, LiF (2 : 3) 1·25 mol. % $NaPO_3$ 0-2 mol. % Na_3PO_4 in NaF, LiF (2 : 3)	700 700	0·06 0·18	0·01 0·5	0·02 0·06	0·05-1 10-80						No connection could be observed between overpotential and PO_4^{---}/PO_3^- ratio.
VI	1·5 mol. % Na_2CO_3 in NaF, LiF (2 : 3)	700	0·065	0·03	0·01	0·05-10	— 0·4 — 0·6	0·5 10	700-800 700-800			The melt contained traces of platinum.
VII	K_2CO_3—Na_2CO_3 (1 : 1)	720	η = 0·19	0·10 I 0·4	0·005 0·01	0-0·15 2-10						The melt contained small amounts of platinum
VIII	1·5 mol. % Na_4SiO_4 1·5 mol. % Na_2SiO_3 in NaF, LiF (2 : 3)	700	0·06	0·2	0·01	0·5-20	— 1·5 — 0·3	40 40	660-720 720-850			
IX	1·5 mol % Na_2O in NaF, LiF (2 : 3)	700	η = 0·215	0·04 I 0·08	0·004 0·01	— 2-4 10-80				18	± 0·5	The melt contained small amounts of platinum
X	1·5 mol. % Na_2O 1·25 mol. % Na_3PO_4 in NaF, LiF (2 : 3)	700	η = η 0·20	0·09 I 0·15 I 0·45	0·005 0·01 0·008	0-0·5 2-0 2-80						The melt contained small amounts of platinum.
XI	1·5 mol. % Na_2O 2·5 mol % Na_3PO_4 in NaF, LiF (2 : 3)	700	η — η — 0·20	0·10 I 0·22 I 0·42	0·005 0·02 0·008	0-0·5 — 1-0 2-80						The melt contained small amounts of platinum.

In a melt of pure Li-Na sulphate the overpotential at 700° c. is of the activated type down to low current densities. At 900° c. both types are found (cp. Fig. 2). A distinctly lower overpotential is found in solutions of sulphate in fluoride, the influence appearing to depend on an expansion of the non-activated section.

The observed effects are in agreement with the assumption that the overpotential in the activated section is determined by reactions of the type

$$SO_4^{--} \rightarrow SO_3 + O + 2e$$
$$PO_4^{---} \rightarrow PO_3^{-} + O + 2e$$

etc. The slope of the $\eta = f$ (log I) curve would then be

$$\frac{RT}{\alpha 2F} \simeq \frac{RT}{F}$$

(where $\alpha = 0{\cdot}5$ and indicates that energy barrier is a symmetrical one for the activated process).

The overpotential would then depend on the bond strength of the oxygen ion in the bond: X — O where X = S, P, C, Si which is in agreement with the observed order. The depressing effect in the overpotential of the fluoride can be explained in different ways, but the experimental material is not yet sufficient for a discussion on the effect.

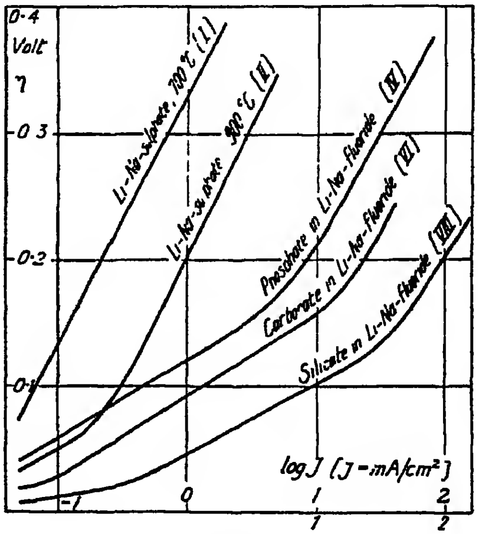

FIG. 2.

In the systems, oxide—Li-Na-fluoride (IX) and pure Na-K carbonate (VII), the overpotential has a different character from that in the systems just described. At low c.d.'s there is a distinct linearity between overpotential and current density. (There is, however, a slight tendency of the platinum to go in solution.)

The characteristic feature of these systems is their high basicity (or O^{--} activity). This perhaps indicates the possible formation of surface oxides which could give rise to the observed potential effect.

In some cases the cathodic overpotential of the oxygen platinum electrode was also examined at low current densities.

In the basic systems (IX), (X), (XI) the variation of the overpotential with the c.d. is linear (the same type as the anodic overpotential). In system IV, however, the overpotential increases rapidly ($\sim RT/F$), and the temperature coefficient is correspondingly high.

The authors express their thanks to Det Videnskapelige Forskningsfond av 1919 and Nansenfondet for grants.

Summary.

The oxygen overpotentials in melts of Li—Na sulphate, and of sulphate, carbonate, phosphate, and silicate dissolved in Na—Li fluoride show some common characteristics. At low c.ds. and high temperatures, the

temperature coefficient of the overpotential is low ($d\eta/dT = -0{\cdot}4$ mv./°c. as is also the variation with the current density $d\eta/d \log I \simeq \frac{RT}{3F}$. At high c.ds. and low temperature, the temperature coefficient

$$(d\eta/dT = -1{\cdot}5 \text{ mv./C°})$$

and the variation with the current density $\left(d\eta/d \log I \simeq \frac{RT}{F}\right)$ are distinctly higher. The overpotential in this region, which seems to be of an activated nature, decreases in the order

$$SO_4^{--} > PO_4^{---} > CO_3^{--} > SiO_4^{----}$$

i.e. parallel with the bond strength of the X—O bond.

In melts of Na carbonate and of alkali oxides dissolved in Na—Li fluoride, the overpotential at high temperature and low c.ds. show a linear variation with the c.d. (η = const. I).

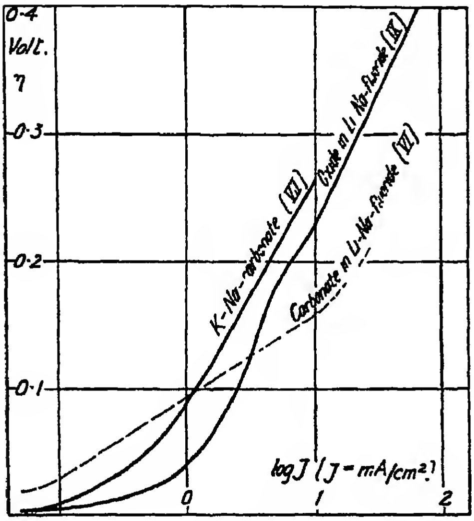

FIG. 3.

Résumé.

Dans le sulfate double de Li et Na fondu et dans le sulfate, le carbonate, le phosphate et le silicate avec le fluorure de Li-Na employé comme fondant, les survoltages d'oxygène montrent quelques caractères communs. A haute température et avec de faibles densités de courant, le coefficient de température du survoltage est faible ($d\eta/dT = -0{\cdot}4$ mv./°c.), de même que la variation avec la densité de courant $\left(d\eta/d \log I \sim \frac{RT}{3F}\right)$. A basse température et avec de hautes densités de courant, le coefficient de température et la variation avec la densité de courant $\left(d\eta/d \log I \sim \frac{RT}{F}\right)$ sont sensiblement supérieurs. Le survoltage, dans cette région qui semble activée, décroît dans l'ordre

$$SO_4^{--} > PO_4^{---} > CO_3^{--} > SiO_4^{----}$$

c'est à dire parallélément à la force de la liaison X—O.

Dans le carbonate de Na fondu et dans les oxydes alcalins dissous dans le fluorure de Li-Na fondu, le survoltage à haute température et faibles densités de courant varie linéairement en fonction de la densité de courant (η = const. I).

Zusammenfassung.

Die Sauerstoffüberspannungen in Schmelzen von Li_2SO_4—Na_2SO_4 und von Lösungen von Sulfat, Karbonat, Phosphat und Silikat in NaF—LiF besitzen mehrere allgemeine Merkmale. Bei niedrigen Stromdichten

und hohen Temperaturen haben sowohl der Temperaturkoeffizient der Überspannung ($d\eta/dT$) als auch die Veränderung der Überspannung mit der Stromdichte ($d\eta/d \log I$) niedrige Werte. Bei höheren Stromdichten und niedrigeren Temperaturen haben diese Derivarte der Überspannung höhere Werte. In diesem Bereich scheint die Überspannung eine Folge von Aktivierung zu sein und nimmt in der Reihenfolge

$$SO_4^{--} > PO_4^{---} > CO_3^{--} > SiO_4^{----}$$

ab, was auch die Reihenfolge der Bindungsfestigkeit der X—O—Bindungen ist.

In Lösungen von Alkalioxyden in geschmolzenem NaF—LiF bei hohen Temperaturen ist die Überspannung bei geringen Stromdichten eine lineare Funktion der Stromdichte.

ELECTRODE REACTIONS IN THE ALUMINIUM REDUCTION CELL.

By T. G. Pearson and J. Waddington.

Received 19*th March*, 1947.

The purpose of this contribution is to record and explain the characteristic features of the electrode reactions in the aluminium reduction cell when it is operating in the normal or " down " condition.

Much of the experimental work and most of the theoretical arguments have already been published,[1] but we justify the present paper by the new evidence on the constitution of molten cryolite electrolytes and on the conductivity of electrolytes containing calcium fluoride, and by the work on the cause of carbon monoxide formation in the anode gases. It also seems desirable to draw together the scattered practical and theoretical work much of which has appeared in journals and in languages not easily accessible to English-speaking workers.

The cell consists essentially of a carbon anode, a molten aluminium cathode, and an electrolyte of molten cryolite in which alumina is dissolved. The overall reaction occurring in the cell consists in the reduction of alumina to aluminium and the oxidation of carbon to its monoxide and dioxide.

When there is sufficient alumina in the electrolyte (commonly termed the " flux ") and the c.d. is not too high, electrolysis proceeds smoothly with the application of 4·5-6·0 v. with the production of aluminium at the cathode and a mixture of carbon dioxide and monoxide at the anode. When there is insufficient alumina in the electrolyte or if the c.d. is increased beyond a critical value depending on the composition of the electrolyte, the nature of the carbon of the anode, and the temperature, the apparent resistance of the cell rises rapidly and the composition of the anode gases alters in that the ratio of carbon dioxide to monoxide diminishes and carbon tetrafluoride appears in considerable quantity. At the same time close inspection of the anode reveals a luminous discharge. The cell is then said to have gone " up " and the applied E.M.F. may be as much as 30 v. before a steady " up state " is reached. In certain circumstances a further increase in c.d. leads to a still higher

[1] Fedotiev, *Electrolysis in Metallurgy* (1934); Fedotiev, *Electrometallurgy*, 2nd ed. (1934); Drossbach, *Z. Elektrochem.*, 1934, 40, 605; Guskov, *Metallurg.*, 1934, 9 (10), 78; Terebesi, *Helv. Chim. Acta*, 1935, 18, 166; Cuthbertson and Waddington, *Trans. Faraday Soc.*, 1936, 32, 745; Tverdovskii and Molchanov, *J. Appl. Chem.* (*U.S.S.R.*), 1937, 10, 1011; Baimakov, Batashev and Evlannikov, *Trans. Leningrad Ind. Inst.*, 1939 (1), 24.

increase in resistance until a third more or less steady condition, known as the " super up state " is reached. The present discussion is confined to the behaviour of the cell in the normal or " down " condition.

The Electrolyte.

The electrolyte consists of a solution of alumina in cryolite which may contain either deliberately or adventitiously calcium fluoride and more aluminium fluoride or sodium fluoride than is represented by the cryolite composition 3 NaF . AlF_3.

There is strong evidence that pure cryolite at its melting point is partially dissociated into aluminium and sodium fluorides (or their ions). The free energy increment for the reaction

$$Na_3AlF_6 \rightleftharpoons 3\,NaF + AlF_3$$

may be derived from the data in Table I.

TABLE I.—THERMAL CONSTANTS OF SODIUM FLUORIDE, ALUMINIUM FLUORIDE AND CRYOLITE.

	Aluminium Fluoride.	Sodium Fluoride.	Cryolite.
Transition temp. °K.	—	—	838 [1(a)]
ΔH Transition, cal. mole.$^{-1}$	—	—	1,400 [1(a)]
Melting point, °K.	1,533 [2]	1,263 [3]	1,280 [4]
ΔH Fusion, cal. mole.$^{-1}$	21,750 [2]	7,000 [5]	15,500 [6]
Entropy ΔS_{298}, cal. mole.$^{-1}$ deg.$^{-1}$	16·5 [2]	13·4 [7]	56·7 [2]
ΔH Formation, cal. mole.$^{-1}$	331,500 [8]	136,600 [9]	761,650 [8]
C_p Liquid, cal. mole.$^{-1}$ deg.$^{-1}$	32 [2]	16 [2]	80 [2]

Specific Heat Equations.

Aluminium fluoride : [10] $C_p = 18{\cdot}578 + 560{\cdot}02 \times 10^{-5}T - 179{\cdot}01 \times 10^3T^{-2}$.
Sodium fluoride [11] : $C_p = 12{\cdot}098 + 189{\cdot}13 \times 10^{-5}T - 195{\cdot}01 \times 10^3T^{-2}$
Cryolite : [12]
Below 838° K. : $C_p = 42{\cdot}133 + 4255{\cdot}9 \times 10^{-5}T - 473{\cdot}50 \times 10^3T^{-2}$.
Above 838° K. : $C_p = -85{\cdot}538 + 14316{\cdot}1 \times 10^{-5}T - 16514 \times 10^3T^{-2}$.

We find that for the molten flux, $\Delta F_T = -33{,}353 + 9{\cdot}0893T$, from which we may compute that cryolite is about 15 % dissociated at 1000° C., the dissociation increasing with rising temperature.

1(a) From data of Roth and Bertram, *Z. Elektrochem.*, 1929, **35**, 105.
2 Estimated.
3 Mean of various published values.
4 Mean of determinations by Mashovets, *J. Appl. Chem. U.S.S.R.*, 1936, **9**, 789, and Lundina, quoted by Mashovets, *The Electrometallurgy of Aluminium* (Russian), 1938.
5 Kelley, *U.S. Bur. Mines Bull.*, 1936, No. 393.
6 Mean of various values from published studies of binary melting point composition curves.
7 From residual ray data, *Landolt-Börnstein, Physikalisch-Chemische Tabellen*, 3rd Supp., 1936, **3**, 758, and estimation.
8 Gmelin, *Handbuch der Anorganischen Chemie, Aluminium, B*, System No. 35, p. 369.
9 Wartenberg, *Z. anorg. Chem.*, 1926, **328**, 151.
10 From data of Lyaschenko, *Metallurg.*, 1935, **11**, 85, quoted by Mashovets, *The Electrometallurgy of Aluminium*.
11 From data of Karetnekov and Krestovnikov, *Legkie Metallurg.*, 1934, **4**, 29, and Lyaschenko, *Metallurg.*, 1935, **11**, 85, quoted by Mashovets, *loc. cit.*
12 From data of Roth and Bertram, *Z. Elektrochem.*, 1929, **35**, 105 ; Karetnekov and Krestovnikov, *loc. cit.* ; and Lyaschenko, *loc. cit.* ; see Mashovets, *loc. cit.*

Confirmation of the order of the dissociation is found in the results of density determinations on molten mixtures of sodium and aluminium fluorides shown in Fig. 1.

The curves each show a maximum value for the density of a melt on the NaF-rich side of the cryolite composition, the hump being flatter, and more displaced towards the NaF-rich side at the higher temperature. These phenomena accord with the assumption that molten cryolite is dissociated and that the dissociation increases with rising temperature, but quantitative interpretation of the results can only be very approximate. Assuming the additivity of molar volumes, and deriving by extrapolation values for the densities of aluminium fluoride and undissociated cryolite, we may construct density-composition curves that satisfactorily fit the observed values by assuming that cryolite is about 20 % dissociated at

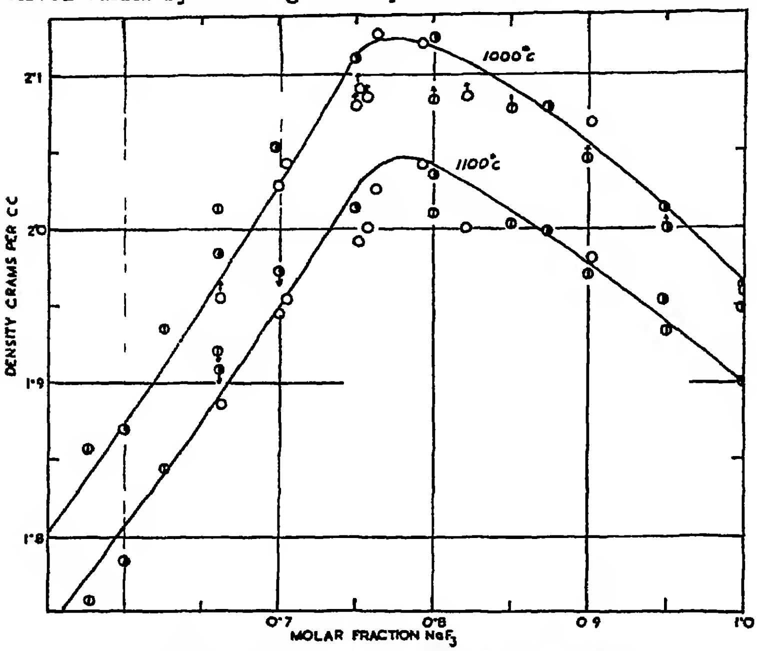

FIG. 1.—Density of molten NaF–AlF_3 fluxes at 1000° and 1100° C.

O British Aluminium Co.

Ⓘ Z. F. Lundina, cited by Mashovets, *Electrometallurgy of Aluminium*.

● G. A. Abramov and P. A. Kozunov, *Trans. Leningrad Ind. Inst.*, 1939, 1, 60.

1000°, and about 30 % dissociated at 1100°. The theoretical curves are the full lines in Fig. 1.

When a layer of molten aluminium is held under a layer of molten cryolite, the aluminium picks up sodium to a definite equilibrium amount which is small or large according as the flux contains more or less aluminium fluoride than is represented by the cryolite composition, and according as the temperature is low or high. The data are shown graphically in Fig. 2.

These data also conform to the assumption that molten cryolite is dissociated to its constituent salts or their ions. Thus, the free energy increment for the reaction

$$AlF_3 + 3\ Na \rightleftharpoons 3\ NaF + Al$$

is found to be given by:

$$\Delta F_T = -\ 72{,}792 - 0{\cdot}5\ .\ 2{\cdot}303\ .\ T \log T + 8{\cdot}422T,$$

leading to a value for the equilibrium constant of $2 \cdot 8 \times 10^{11}$ at 1273° K. Since the sodium content of the aluminium in equilibrium with the flux is known to be small, we may assume very approximately that the molar fractions of sodium fluoride, aluminium fluoride and cryolite in the flux in the presence of aluminium are similar to those in the absence of aluminium, and we may substitute such molar fractions, which are readily computed for various arbitrary degrees of dissociation of cryolite, in the equilibrium equation to calculate the sodium content of the aluminium in equilibrium with the flux. The curves derived in this way assuming that pure cryolite is (*a*) 20 %, (*b*) 35 %, and (*c*) 50 % dissociated are shown in Fig. 2. They show the correct trend for the effect of flux composition on the sodium content of the aluminium; quantitative agreement is scarcely to be expected in view of the errors in the experimental data and the approximate nature of the theoretical treatment.

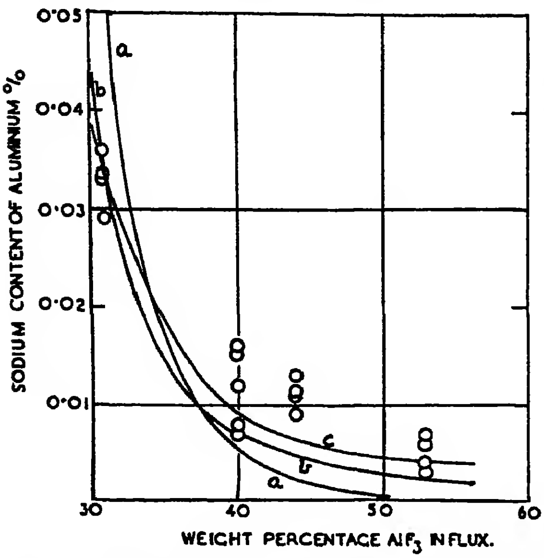

FIG. 2.—Sodium content of aluminium in contact with NaF–AlF_3 fluxes at 1000° C.

(*a*) Cryolite, 20 % diss. (*b*) Cryolite, 35 % diss. (*c*) Cryolite, 50 % diss.

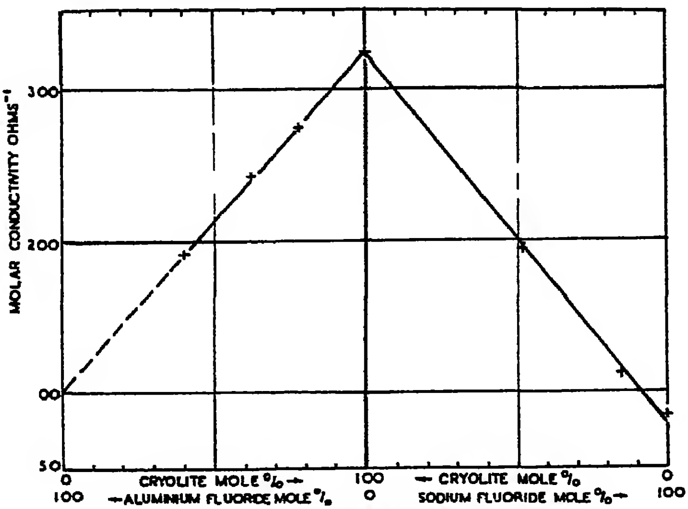

FIG. 3.—Conductivity of NaF–AlF_3 fluxes at 1000° C.

It would thus seem reasonable to consider a molten cryolite flux as a mixture of cryolite, sodium fluoride, and aluminium fluoride or of their ions.

Conduction in the Electrolyte.

The electrical conductivities of molten fluxes of the type used in the reduction cell have been measured by a number of workers.[13] Where comparable measurements have been made, the absolute values of conductivity are in very poor agreement, differing in some cases by as much as 50 %, due no doubt to the inherent difficulty in measuring the conductivities of corrosive, decomposible, oxidisable fluxes near 1000° C., difficulties that we can confirm from experiments made in these laboratories. On the other hand, the trends of the effect of the various constituents on the conductivity of cryolite are surprisingly consistent, so that it will be sufficient to record for each constituent only one set of values, which

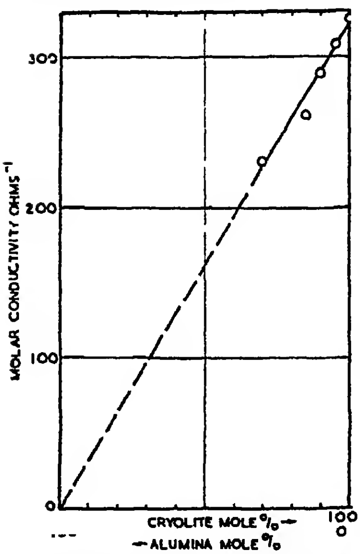

FIG. 4.—Conductivity of cryolite–Al_2O_3 fluxes at 1000° C.

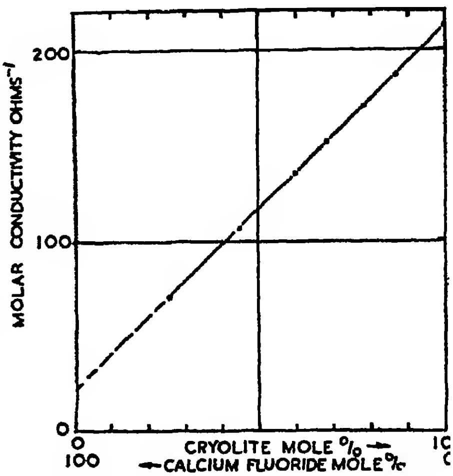

FIG. 5.—Conductivity of cryolite–CaF_2 fluxes at 1000° C.

will be those most recently determined for want of a better criterion of reliability.

The data are shown in Fig. 3, 4 and 5, their origin being as follows: specific conductivity of NaF—AlF_3 and cryolite—Al_2O_3 fluxes; [14] density of cryolite—Al_2O_3 fluxes; [15] the conductivity and density of cryolite—CaF_2 and the density of NaF—AlF_3 fluxes were measured in these laboratories.

It may be seen that the extrapolated value of the molar conductivity of alumina is zero, and of calcium fluoride is very small in comparison with the conductivity of cryolite and sodium fluoride. In view of the low conductivity of calcium fluoride, it would seem that little current is

[13] Richards, *Electrochem. Ind.*, 1903 **1**, 158; Allmand, *Fundamentals of Applied Electrochemistry* (1934), p. 266; Pascal and Jouniaux, *Bull. Soc. Chim.*, 1913, **13**, 439; Arndt and Kalass, *Z. Elektrochem.*, 1924, **30**, 12; Cuthbertson and Waddington, *Trans. Faraday Soc.*, 1936, **32**, 745; Parravano and D'Agostino, *Atti. Acad. Lincei*, 1932, **16**, 185; Batashev, *Leghie Metally*, 1936, **10**, 48.

[14] Batashev, *loc. cit.*, cited by Mashovets, *The Electrometallurgy of Aluminium*.

[15] Lundina, *Trans. All-Union Aluminium and Magnesium Institute*, 1936, **13**, 5; and Abramov, *Leghie Metallurg*, 1936, **11**, 27, cited by Mashovets.

carried by the fluoride ion. Since also the equivalent conductivity of cryolite, 107 mhos, is little greater than that of sodium fluoride, 86 mhos, it is reasonable to assume that most of the current in the cryolite fluxes used in the aluminium reduction cell, the composition of which in respect of NaF and AlF_3 departs but little from that of cryolite, is carried by the sodium ion, a view consistent with the considerable migration of sodium to the cathode during the electrolysis of cryolite (see below).

The relatively high conductivity of aluminium fluoride indicated by extrapolation of the cryolite-AlF_3 conductivity-composition curve is surprising in comparison with the negligible conductivities of the other halides of aluminium.

Baymakov, Batashev and Evlannikov [16] electrolysed cryolite-alumina melts in a graphite cell, which acted as one electrode, fitted with a sintered alumina pot as a diaphragm and containing the other electrode. Using a magnetite rod as the anode, and an electrolyte of cryolite saturated with alumina at a temperature of 980-990° c., the following typical data were obtained in an experiment.

TABLE III.—TRANSPORT EXPERIMENTS IN CRYOLITE FLUXES.

Duration of Electrolysis. Hr.	Current Passed. Amp. hr	Analysis of Anolyte.			Rational Composition of Anolyte.			
		Na %	Al %	F %	Na_3AlF_6 %	NaF %	AlF_3 %	Al_2O_3 %
0	0	28·8	18·2	46·2	81·6	3·9	—	14·5
2	6	25·2	19·8	50	76·7	—	12·3	11·4

In other experiments in which a chromium rod was used as the cathode, the change in composition of the electrolyte was as follows:

TABLE IV.—TRANSPORT EXPERIMENTS IN CRYOLTIE FLUXES.

Duration of Electrolysis. Hr.	Current Passed. Amp. hr.	Analysis of Catholyte.			Rational Composition of Catholyte.			
		Na %	Al %	F %	NaO %	Na_3AlF_6 %	NaF %	Al_2O_3 %
0	0	28·8	18·2	46·2	0	81·6	3·9	14·5
2	4	39·8	11·6	42·1	1·3	36·8	48·8	12·9

From a large number of similar experiments, and of supplementary experiments in which the catholyte was kept separate from the anolyte in a specially constructed cell with only a narrow communicating channel between the compartments, the following general conclusions were drawn. The cathode space is noticeably enriched in sodium and impoverished in aluminium, whilst the fluorine content remains unchanged or decreases slightly. If the change in the catholyte composition is expressed rationally the results show generally an excess of sodium fluoride in the catholyte, which may amount to as much as 50 %. In the majority of the experiments the alumina content was lower than in the original electrolyte, and approximately equal to or slightly lower than that in the anolyte. The catholytes showed a distinct alkalinity which varied between 0·1 % and 3·9 %.

The anode space is appreciably impoverished in sodium and enriched in aluminium while remaining unchanged or only slightly enriched in respect of fluorine. From the point of view of rational composition the

[16] *Trans. Leningrad Ind. Inst.*, 1939, 1, 34.

anolytes contained an excess of aluminium fluoride which in certain cases amounted to as much as 23 %. In general sodium fluoride was much less than in the catholyte or the original electrolyte. In the majority of experiments the aluminium oxide content of the anolyte was greater than that of the catholyte and less than or equal to the aluminium oxide content of the original electrolyte. As a rule all the anolytes were neutral to indicators.

These results, together with those from the conductivity measurements, are consistent with the view that the sodium ion takes a predominant part in transporting the current across the electrolyte, and that the AlF_6''' ion is also present and moves towards the anode. Alumina and calcium fluoride play a negligible part in transporting the current.

The Cathode Reaction.

Considerable light was thrown on the processes occurring at the cathode by Belyaev's [17] measurements of the decomposition voltages of various cryolite fluxes. He measured the decomposition potentials of Na_3AlF_6, K_3AlF_6, and Li_3AlF_6, in the presence and absence of alumina by the current-potential curve method using platinum electrodes and a partitioned graphite cell. The results obtained are given in Table V.

TABLE V.—DECOMPOSITION VOLTAGES OF CRYOLITE FLUXES.

Electrolyte.	Decomposition Voltage. At 950° C.	Decomposition Voltage. At 1080° C.	Electrolyte.	Decomposition Voltage at 1080° C.
Na_3AlF_6 + 15 % Al_2O_3 .	2·22	2·01	Na_3AlF_6	2·07
K_3AlF_6 + 15 % Al_2O_3 .	2·20	2·01	K_3AlF_6	2·13
Li_3AlF_6 + 7 % Al_2O_3 .	2·20	2·03	Li_3AlF_6	2·20

These figures agree reasonably with the determinations of Cuthbertson and Waddington,[18] who obtained 2·23 v. and 2·20 v. respectively, for the decomposition voltages of cryolite and cryolite containing about 15 % alumina. It will be seen from the table that the decomposition potential of cryolite-alumina melts has a constant value of about 2·2 v. at 950° c. and 2·01 v. at 1080° c., independent of the cation. The cathodic process is therefore probably the same in all cases, and consists in the discharge of aluminium ions, which may be produced either by the dissociation of Al_2O_3 (possibly $Al^{\cdots} + AlO_3'''$) or by the dissociation of AlF_6 (possibly $Al^{\cdots}$ and AlF_6'''). The data on the decomposition potential of the cryolites in the absence of alumina allow us to discriminate between these alternatives, for some aluminium fluoride is present in even a pure cryolite flux, and one might expect, therefore, to obtain the same value for the decomposition voltage as in the presence of alumina, or at the least a value independent of the alkali metal in the cryolite. Such is not the case, however, for the decomposition potential differs for the different cryolites, the primary cathodic process evidently consisting in the discharge of the alkali metal ion.

Thus, the difference in decomposition potential of the different cryolites provides ground for the assumption that the aluminium ions, the discharge of which constitutes the cathodic process in normal electrolysis of cryolite alumina melts, are the result of the dissociation of Al_2O_3. Under certain conditions, as for example, in an unstirred melt, the accumulation of a high concentration of sodium ions near the cathode may favour the primary evolution of this element, so that the possibility of a preferential primary

[17] *Tsvet. Met.*, 1938, 7, 87. [18] *Trans. Faraday, Soc.*, 1936, 32, 745.

deposition of sodium, or of a simultaneous primary deposition of aluminium and sodium in amounts proportional to their activities and decomposition potentials is not excluded.

The Anode Reaction.

Belyaev's experiments do not enable us to determine the nature of the primary anodic process, but the fact that oxygen is the species deposited is consistent with the view expressed by him, and earlier by Fedotiev, that the current transported to the anode proceeds by way of the AlF_6''' ion, but that the ion primarily discharged is AlO_3'''. The analogy with the electrolysis of acids and bases in aqueous solution is thus close, the slightly ionised alumina corresponding with water, thus

$$Al_2O_3 \rightleftharpoons Al^{\cdot\cdot\cdot} + AlO_3'''$$
$$2\ AlO_3''' = Al_2O_3 + 1\tfrac{1}{2}O_2 + 6e.$$

The subsequent fate of the oxygen is of considerable importance in the practical operation of the cell.

During the normal working of the cell the anode gases consist of 70-90 % CO_2 and 10-30 % CO, and for a given cell in good condition the proportion of the two gases remains constant within 2-3 %. At the "up" the proportion of CO_2 rapidly falls to 20-40 %, the CO rises to 40-60 %, and volatile fluorine compounds consisting largely of CF_4 form 15-30 % of the gas.

It seems likely that in the down condition oxygen must be deposited at the anode with 100 % current efficiency for there are no indications of appreciable quantities of any other anodic products but CO_2 and CO during normal running. In an endeavour to confirm this mechanism, experiments were carried out in which 2 in. cubes of well-baked dense carbon or graphite were used as anodes in a cell consisting of a graphite crucible containing a molten flux of 80 % cryolite, 15 % calcium fluoride and 5 % aluminium fluoride to which sufficient alumina was added to prevent the anode going "up" at any time. Precautions were taken to prevent the air oxidation of the upper surface of the cubes by painting them with phosphoric acid and protecting further with a layer of solidified flux.

In some 36 experiments the loss in weight of carbon was found to be approximately equal to the theoretical amount necessary for 100 % CO_2 production at the anode at 100 % anode current deficiency, the average values lying between 101 and 105 %. In view of the probable occurrence of slight aerial oxidation and of disintegration of the anode material by the flux, these results cannot be said to differ significantly from 100 %. If, however, the 25-30 % of CO usually found in the anode gases had arisen as a primary product, the loss in carbon would have been 15 % greater. It is therefore likely that the primary gaseous product at the anode is CO_2.

An independent line of reasoning leads to a similar conclusion. A mixture of CO_2 and CO deposited at the anode would tend to be in equilibrium with carbon and with oxygen according to the equilibria :

$$C + CO_2 \rightleftharpoons 2CO \quad . \quad . \quad . \quad . \quad (1)$$
$$2CO + O_2 \rightleftharpoons 2CO_2. \quad . \quad . \quad . \quad . \quad (2)$$

The mixture cannot be in equilibrium with both at the same time unless the oxygen pressure is exceedingly small (less than 10^{-15} atmos.). The composition of the mixture would therefore depend upon the velocities of the reactions. The oxidation of CO is almost instantaneous at about 1000° c., whereas the reduction of CO_2, even on 5 mm. coke particles, proceeds with a measurable velocity given approximately by the relationship [19]

$$0{\cdot}01t = \log (1/1 - x)$$

[19] *Bur. Mines Bull.*, 1911, No. 7, 22.

where t is the time of contact and x is the fraction of CO produced from pure CO_2 at time t. Thus even for a contact time of 1 sec. the resulting gas would contain only $2\frac{1}{2}$ % CO. Thus the oxidation of CO would be expected to be the dominant factor.

As the free energy required to deposit the oxygen increases with the oxygen pressure the decomposition voltage will also increase. The theoretical decomposition voltage for the aluminium cell is 2·15 v. at 980° c. if oxygen at atmospheric pressure is the primary product at the anode. The oxygen pressure is, however, considerably below atmospheric, being reduced by the above reactions. The anode is thus depolarised and the decomposition voltage reduced. It may be shown [20] that:

$$\text{depolarisation (in volts)} = \frac{0{\cdot}002T}{4} \log \frac{1}{pO_2}$$

where T is the absolute temperature and pO_2 the oxygen pressure, from which the CO_2, CO ratio in the gas phase in equilibrium with the oxygen may be calculated using:

$$\frac{pCO_2}{pCO} = \sqrt{KpO_2}$$

where K is the equilibrium constant of reaction (2) given by

$$\log K = \frac{28600}{T} - 8{\cdot}46.$$

The following results have been obtained for a temperature of 980° c. using Drossbach's equations:

Decomposition Voltage (v.).	Depolarisation (v.).	Log pO_2	% O_2	% CO_2	% CO
2·15	0	0	100	0	—
1·95	0·2	− 3·19	0·07	99·93	—
1·75	0·4	− 6·38	—	100·0	—
1·55	0·6	− 9·58	—	99·6	0·4
1·35	0·8	−12·75	—	86·0	14·0
1·20	0·95	−15·15	—	29·0	71·0

As pointed out above the reduction of CO_2 is probably comparatively slow, so that equilibrium will only be approached when the rate of production of CO_2 is low, i.e. when the c.d. is small. As the c.d. is increased the CO_2 pressure and consequently the oxygen pressure will gradually build up and since the decomposition voltage is dependent upon the oxygen pressure this will also increase with increasing c.d. According to the above table, appreciable quantities of CO will only be present in the anode gases if the c.d. is such that the decomposition voltage is below about 1·55 v. Actual measurements of the decomposition voltage of a reduction furnace indicate this to be about 1·7 v. which would therefore indicate that practically 100 % CO_2 was the initial product. A lower decomposition voltage, a greater depolarisation and the presence of an appreciable percentage of CO in the anode gases could only be obtained by decreasing to a considerable extent the anode c.d.

Drossbach in his laboratory experiments found that the decomposition voltage and the CO_2 content of the anode gases increased as the anode c.d. was raised to about 3·2 amp./sq. in., but beyond this value the c.d. had little effect on the CO_2 content, which remained steady at about 86 % although the decomposition voltage continued to increase. This CO_2 content of 86 % in the gases collected probably corresponded to 100 % in the gases as formed at the anode for not only were the gases drawn off

[20] Drossbach, *Z. Elektrochem.*, 1936, 42, 65.

through a refractory tube surrounding the carbon rod used as anode thus permitting some reduction of the CO_2, but also, as we shall see later, some CO_2 was probably reduced by metal fog. As the anode c.d. of an actual reduction furnace is usually considerably greater than 3·2 amp./sq. in. we should expect the initial anode product to be almost 100 % CO_2.

There are therefore several reasons why it is thought that CO_2 is the initial anode product although the gases escaping from the furnace contain varying amounts of CO which cannot be completely accounted for by the reduction of CO_2 by the carbon of the anode. The cause of the CO formation is thus to be sought elsewhere.

Just as it is difficult to see how oxygen can be deposited at less than 100 % current efficiency it is equally difficult to see how the total metal, sodium and aluminium, actually formed at the cathode surface can be produced at anything other than 100 % current efficiency. But the average metal yield of a furnace may easily correspond to no more than 85 % current efficiency, and the oxygen yield must clearly be equivalent to this aluminium if the elementary laws of chemistry are to be satisfied, for the overall process occurring consists essentially in splitting the alumina into aluminium and oxygen. The inefficiency of a furnace must therefore result from the interaction of the electrode products, the metal lost from the cathode combining with an equivalent amount of oxygen from the anode. This we believe to be due to the diffusion of a metal fog from the cathode surface to the anode, where it reduces an almost equivalent amount of CO_2 to CO, the remainder being oxidised by the air.

The formation of metal fogs during the electrolysis of fused salts has been studied by a number of workers.[21]

When a particle of aluminium is dropped into a pot of clear molten cryolite streamers of fog can be seen spreading from the metal through the flux. If no more metal is added this fog can be removed by prolonged heating but so long as any metal remains the flux cannot be cleared at any temperature. It is presumed that the fog oxidises at the surface of the flux and that the oxidation products are soluble in the flux. As regards the nature of the fog, there seem to be only two possibilities, sodium and aluminium, and the former of these is the more probable for the vapour pressure of aluminium at 1000° C. is only 0·6 mm. of mercury whilst that of sodium is over 1000 mm. Moreover, the amount of fog observed at any given temperature increases with the sodium fluoride content of the flux, as would be expected from the discussion of the flux equilibria outlined above. Very little fog is formed in fluxes rich in aluminium fluoride whilst dense fog is produced in NaF-rich fluxes and even when pure sodium fluoride is electrolysed. We consider it probable that the fog consists of a dispersion of very small bubbles of sodium vapour.

The fog formed at the cathode diffuses or is carried towards the anode by the circulating flux and is probably oxidised there by the anode gas. Both sodium and aluminium can reduce CO_2 at the temperature of the reduction furnace although aluminium tends to form the carbide particularly if the supply of CO_2 is limited. As there is excess of gas the reaction will occur with the reduction of CO_2 to CO. The fog probably does not reach the anode itself but reacts with the froth of gas bubbles surrounding the anode. The flux carried up to the surface of the bath by the rising gas bubbles will contain very little fog and some of this may be oxidised at the surface by the gases held beneath the crust. If the fog is aluminium the oxidation product, alumina, will dissolve in the flux whilst if the fog is sodium the Na_2O formed will react with the aluminium fluoride constituent of the flux producing alumina :

$$3\,Na_2O + 2\,AlF_3 = 6\,NaF + Al_2O_3.$$

[21] e.g. Lorentz, *Der Elektrolyse Geschmolzener Salze*, p. 40 ; Ruff and Busch, *Z. anorg. Chem.*, 1925, 144, 87 ; Drossbach, *Z. Elektrochem.*, 1936, 42, 65 ; *Trans. Amer. Electrochem. Soc.*, 1935, 52, 249.

In either case we get, in effect, the recombination of the original electrode products to give alumina. Thus although metal and oxygen are both deposited at the electrodes at 100 % efficiency and an equivalent amount of carbon is used, the oxygen in the gases passing out of the furnace will be equivalent to the actual metal yield corresponding with the efficiency of the cell. On the basis of this explanation it may be shown that the CO_2 content of the anode gases should be equal to $2x - 100$, where x is the percentage current efficiency.

A number of experiments tends to confirm this explanation. To ascertain the nature of the fog, two cryolite fluxes were held molten in two graphite crucibles. In one crucible the flux was clear but in the other it was fogged from a layer of aluminium in the bottom of the crucible. A small graphite ladle containing molten lead was held in each flux for a given time. The analysis of the lead samples given in Table VI show that

TABLE VI.—SODIUM CONTENT OF LEAD IN PRESENCE OF FOGGED AND CLEAR FLUXES.

Length of Time for which Lead was held in Molten Flux (hr.).	Sodium Content of Lead.	
	Unfogged Flux. %	Fogged Flux. %
1	0·007	0·075
3	0·006	0·49

sodium has been absorbed from the fogged flux. The lead, being more noble than either sodium or aluminium, is incapable of reducing their compounds and therefore of absorbing either metal from the flux alone, yet in the fogged flux sodium has accumulated in the lead. Metal in some form must therefore have diffused from the layer of aluminium in the bottom of the crucible through the flux to the lead. It seems probable, therefore, that the fog consists either of metallic aluminium or sodium, for aluminium could produce sodium at the flux lead interface by reaction with the sodium compounds in the flux. On the other hand, the observation that the density of the fog increases with the sodium fluoride content of the flux tends to show that the fog is metallic sodium liberated by reaction between aluminium and sodium fluoride. The slow rate of increase of the sodium content of the lead is an indication that the percentage by weight of fog in the flux is small, and it is probably for this reason that direct attempts to identify sodium in chilled samples of the flux fails. It may readily be shown that a stationary concentration of as little as 0·005 % Na in the flux of a reduction cell is sufficient to account for a drop in cathode current efficiency of over 20 %.

The effect of the fog on the composition of the anode gas has been demonstrated by collecting the anode gases during the electrolysis of fogged and comparatively unfogged fluxes of identical composition. Since it is almost impossible to arrange an electrolysis in which the flux does not become fogged, fog-free conditions were simulated by beginning with a clear flux and electrolysing for a very short period, interrupting the collection of gas and the current to allow the flux to clear, and repeating the procedure until sufficient gas had been collected for analysis. In a typical experiment, the ratio CO_2/CO was 1·85 in the gases from the unfogged flux, and 0·59 in the gases from the fogged flux.

It did not appear practical to make quantitative measurements of the current efficiency in the laboratory to correlate the anode gas composition with metal production efficiency, but a series of observations on reduction furnaces, of which the following results are typical, confirmed that such a correlation did in fact exist. Three furnaces were selected

in which the cathode current efficiencies were estimated from the metal yields, and the percentage of CO_2 corresponding with these current efficiencies were compared with that actually found by gas analysis. Typical data are shown in Table VII.

TABLE VII.—RELATIONSHIP BETWEEN CO_2 CONTENT OF ANODE GASES AND CURRENT EFFICIENCY.

Furnace No.	Current Efficiency.	Corresponding % CO_2 in Anode Gas.	CO_2 found during "Inter-up" Period, %.
1	85	71	69
2	83	66	62
3	72	45	32

Agreement must be considered satisfactory bearing in mind the disturbing features present in the large furnace e.g. the reduction of the CO_2 content of the anode gases by reaction with the anode and the splashing of metal causing direct shorting of the electrodes. Furnace 3 was also in very bad condition, and was showing a considerable amount of luminous flame at the flux surface.

The theoretical and experimental treatment just outlined thus leads to the following general conclusions: (1) the initial anode product is practically 100 % CO_2 at 100 % current efficiency; (2) the oxygen passing out of the furnace as CO_2 and CO is approximately equivalent to the aluminium produced at the cathode; (3) the aluminium current inefficiency at the cathode is mainly due the formation of a metallic fog which is probably sodium; (4) the fog diffuses or is carried to the anode by the circulating flux, and there reacts in the main with the CO_2 reducing it to CO, but also to a slight extent with the atmosphere with the formation of the metallic oxide. The oxidation product by reaction with the flux forms alumina again. The CO_2 content of the anode gases is thus determined by the current efficiency at which the cell is operating, and should be given by the relationship:

metal current efficiency % = $\frac{1}{2}$ (% CO_2 content of anode gases) + 50.

Discussion and Summary.

The cell consists essentially of a carbon anode, a molten aluminium cathode, and an electrolyte of molten cryolite in which alumina is dissolved. The overall reaction occurring in the cell consists in the reduction of alumina to aluminium and the oxidation of carbon to its monoxide and dioxide.

The electrolyte may contain in addition to cryolite and alumina, either adventitiously or deliberately, calcium fluoride and more aluminium fluoride or sodium fluoride than is represented by the cryolite composition; the cryolite itself is also partially dissociated into its constituent salts or their ions at the working temperature of about 1000° c. Neither the alumina nor the calcium fluoride play an appreciable part in transporting the current, the majority of which is carried by the sodium cation. Some transport to the anode probably occurs via the anion AlF_6''' derived from cryolite or aluminium fluoride:

$$Na_3AlF_6 \rightleftharpoons 3\,Na^{\bullet} + AlF_6'''$$
$$Al_2F_6 \rightleftharpoons Al^{\bullet\bullet\bullet} + AlF_6'''.$$

At the cathode during the normal operation of the cell, the ion primarily discharged appears to be aluminium derived largely from the dissociation of alumina:

$$Al_2O_3 \rightleftharpoons Al^{\bullet\bullet\bullet} + AlO_3'''.$$

Under suitable conditions a primary deposition of sodium ion may occur, the sodium then reacting with the flux to produce aluminium. The relative extent of the primary depositions of aluminium and sodium must clearly depend on the activities of the ions in the vicinity of the cathode, and their deposition potentials.

At the anode, again during the normal operation of the cell, the ion primarily deposited would appear to be AlO_3''' derived from the dissociation of the alumina. On deposition this ion may either yield alumina and oxygen :

$$2\ AlO_3''' = Al_2O_3 + 1\tfrac{1}{2}O_2 + 6e,$$

the oxygen immediately reacting with the carbon of the anode to give CO_2, or the ion AlO_3''' may deposit and react simultaneously with the carbon according to the equation: $2AlO_3''' + 1\tfrac{1}{2}C = Al_2O_3 + 1\tfrac{1}{2}CO_2 + 6e$. In either case, the gaseous product appears to be CO_2, which is partially reduced to CO (*a*) largely by the metallic fog which is produced at the cathode, and which very probably consists of minute bubbles of sodium vapour, and (*b*) to a much less extent by the carbon of the anode :

$$CO_2 + 2Na = CO + Na_2O$$
$$CO_2 + C = 2CO.$$

The production of metallic fog occurs in the absence of electrolysis through the reaction of metallic aluminium with the flux, the tendency for fog production being greatest in NaF-rich fluxes :

$$Al + 3NaF \rightleftharpoons 3Na + AlF_3.$$

Whether produced in this way, or by primary electrolytic deposition, its effect is the same, namely, to reduce the cathode current efficiency of aluminium production, for any sodium that escapes reaction with flux to produce metallic aluminium at the cathode is carried to the anode where it either reduces some of the anode product CO_2, or is oxidised by the atmosphere, in both cases to form sodium monoxide. The sodium monoxide then re-forms alumina in the flux according to the reaction :

$$3Na_2O + 2AlF_3 \rightleftharpoons Al_2O_3 + 6NaF.$$

If the fog were to consist of aluminium, which seems unlikely, the same end effect would be produced directly, i.e. the re-formation of alumina.

This explanation of the mechanism of CO formation at the anode is confirmed by the observation that :

metal current efficiency % = $\tfrac{1}{2}$ (CO_2 content of anode gases %) + 50.

The arguments advanced have been confined to the cell running in the "down" condition. In the "up" and "super up" states, which have been less fully studied and which are characterised by the condition that the flux is, relative to the c.d. and condition of the anode, impoverished in alumina, the predominant primary anodic and cathodic processes can clearly differ from the normal ones. Thus, there is a higher probability of the primary deposition of the AlF_6''' ion at the anode with the subsequent formation of CF_4, and of the deposition of sodium at the cathode.

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Résumé.

A l'aide de faits expérimentaux, précédemment publiés ou nouveaux, on explique les traits caractéristiques des processus électrochimiques qui prennent place dans la cellule à réduction d'alumine lorsqu'elle fonctionne dans des conditions normales. Les faits expérimentaux nouveaux se rapportent à la constitution d'électrodes de cryolite fondue, à la conductivité d'électrolytes de cryolite contenant du fluorure de calcium et à la présence d'oxyde de carbone dans les gaz anodiques.

Zusammenfassung.

Die charakteristischen Züge der elektrochemischen Prozesse, die bei der elektrolytischen Aluminiumreduktion stattfinden, werden unter Zuhilfenahme von veröffentlichten und neuen Versuchsergebnissen erklärt. Die neuen Daten betreffen die Zusammensetzung von geschmolzenen Kryolithelektroden, die Leitfähigkeit von Kryolithelektrolyten, die Kalziumfluorid enthalten, und die Gegenwart von Kohlenmonoxyd in den Anodengasen.

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THE USE OF SILVER—SILVER CHLORIDE REFERENCE ELECTRODES IN DILUTE SOLUTIONS.

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In the course of certain work on the corrosion of zinc and galvanised iron in dilute solutions it became necessary to select a reference electrode satisfying the following conditions: (i) the electrode should be easily prepared, and reproducible to about 1 mv.; (ii) the electrode should be capable of easy incorporation into cells to be maintained at temperatures up to 85° C., and should behave satisfactorily at such temperatures; (iii) the electrode potential should remain constant under these conditions over long periods of time—up to many months; and (iv) no contaminating substances should be introduced into the solution in amounts sufficient to affect appreciably the corrosion of specimens of zinc, iron, etc., as a result of incorporation of the electrode. These requirements rendered the use of any simple bridge system unsuitable. Since most of the solutions being examined contained some dissolved chloride, the Ag/AgCl electrode was chosen as appropriate for the work.

On consideration of the results obtained some doubt emerged as to the basis on which potential measurements made at different temperatures should be compared. One of the objects of the work was to obtain information about the change in character of surface films on corroding metal specimens and any tendency for such films to break down or reform, etc., as the temperature changed, and it was therefore desirable that the potential measurements made should be truly comparable.

By the usual convention the hydrogen electrode with hydrogen at 1 atmos., and in a solution containing hydrogen ions at unit activity is arbitrarily assumed to be of zero potential at all temperatures. There seems to be no reason why the potential of the hydrogen electrode should not actually change with temperature with respect to its value at some fixed temperature such as 20° C. If this is so, potentials measured at different temperatures would not be directly comparable since measurements at any temperature are always referred to a hydrogen electrode at that temperature. This difficulty could only be overcome by measurements of cells in which the two electrodes are at different temperatures. The existence of liquid junction potentials affects any such determinations and there are other complicating factors in such a cell. Some measurements have been made on cells of this type, but the interpretation of the

results is a matter of some difficulty. It is in fact possible that no useful information can be derived from the results but corrosion studies would be facilitated if potential measurements made at different temperatures could be directly compared and it is felt that discussion along these lines would serve a useful purpose.

Experimental.

The Ag AgCl electrodes used were immersed in the actual corroding solution under investigation and therefore no corrections for junction potentials had to be applied.[1] The only contaminating substance introduced was AgCl, the solubility of which is very small. Moreover, it was considered that dissolved AgCl was probably confined to the liquid within the beaks fitted to the electrodes, and did not easily diffuse into the bulk of the liquid in the vessel. Although tests were run for many months, the liquid in the vessels was changed after intervals of, at most, 4 days and there was therefore little chance of accumulation of the dissolved AgCl. Nevertheless, in view of the very small amounts of dissolved copper salts, for example, which can cause increased localised attack on zinc surfaces it is perhaps a little surprising that incorporation of Ag/AgCl electrodes in the cells has never been observed to have caused any appreciably increased attack of zinc specimens.

Several different methods of preparing Ag/AgCl electrodes on platinum spirals sealed into the glass holders used were investigated including: (1) decomposing a paste of Ag_2O and $AgClO_3$, (2) electrolytic deposition of Ag from a cyanide solution followed by formation of AgCl by electrolysis in dil. HCl, (3) decomposition of Ag_2O paste followed by formation of AgCl by electrolysis in dil. HCl. The last method proved most satisfactory and the procedure finally adopted was as follows.

Spirals of 30 S.W.G. Pt wire were wound to a diameter of about 1 mm. and a length of 1 cm. and sealed into the glass holders. The spirals were uniformly coated with a paste of Ag_2O and water which was decomposed by heating for a short time at 350° C. The resulting silver coating was covered with chloride by electrolysis in N./10 HCl with a current of 2-3 ma. for 2 hr., the Ag electrode being made the anode.

There is some divergence of opinion as to whether light materially affects the potential of Ag/AgCl electrodes,[2] but as extreme accuracy of measurement was not necessary in the present work no attempt was made to prepare and use the Ag/AgCl electrodes completely in the dark. During the greater part of their lives they were, however, operating in the dark.

The solutions under investigation usually contained 30-40 p.p.m. chloride. One supply water for instance contained 41 p.p.m. chloride and this figure was practically constant, and, moreover, did not change appreciably after iron or zinc electrodes had corroded in it for some time. It was found that this small amount of chloride was sufficient to cause Ag/AgCl electrodes to give rise to a constant and reproducible potential, which corresponded to the theoretical value.

Significance of Observed Electrode Potentials.

(1) Concentration of Solution.—The potential of Ag/AgCl electrodes is given by the equation

$$E = E^\circ - \frac{RT}{F}\log_e(a_{\mathrm{Cl}^-}) \quad . \quad . \quad . \quad (1)$$

(a_{Cl^-}) being the activity of the chloride in solution, which, in the dilute solutions considered, is nearly equal to the concentration. The mean activity coefficient for 0·001 N. KCl is about 0·977. The value of E°,

[1] Gilbert, *J. Sci. Instr.*, 1945, **22**, 235.
[2] e.g. Carmody, *J. Amer. Chem. Soc.*, 1929, **51**, 2901.

the potential of an Ag/AgCl electrode in a solution in which $(a_{Cl^-}) = 1$, is 0·22239 v. at 25° c. according to Harned and Ehlers,[3] and at 20° c. is 0·2255 v.

Substituting in equation (1) for a solution containing 41 p.p.m. chloride

$$E_{20°} = +\ 0{\cdot}396 \text{ v.}$$

When electrodes were immersed in either the supply water or KCl solution containing 41 p.p.m. chloride, they usually gave this theoretical value, i.e. the potential was 0·114 v. against a normal calomel electrode, or 0·150 v. against a saturated calomel electrode (at 20° c.). Any electrode diverging more than 1-2 mv. was discarded. (Calculation of the junction potentials for cells comprising N. calomel or saturated calomel, and Ag/AgCl, in the dilute solutions used indicated values of the order of 1 mv.)

Ag/AgCl electrodes have been used in solutions containing as little chloride as 10 p.p.m., in which the theoretical values (+ 0·432 v. against hydrogen at 20° c.) is still given. In such dilute solutions it is necessary to immerse the electrode for some minutes before equilibrium is reached.

(2) Effect of Temperature Variation.—The variation of the standard electrode potential of the Ag/AgCl electrode with temperature between 0° and 60° c. has been given by Harned and Ehlers [4] by equation (2)

$$E^{\circ}_t = 0{\cdot}22239 - 645{\cdot}52 \times 10^{-6}(t - 25) - 3{\cdot}284 \times 10^{-6}(t - 25)^2 + 9{\cdot}48 \times 10^{-9}(t - 25)^3 \quad (2)$$

From this equation E° can be calculated for any temperature between 0° and 60° c. Therefore the potential of the Ag AgCl electrode in a solution containing any concentration of chloride ions can be calculated for any temperature between 0° and 60° c., providing the activity of the chloride ions in the solution at the particular temperature is known.

If it is assumed that equation (2) holds up to 85° c. the potential of the Ag/AgCl electrode in the supply water containing 41 p.p.m. chloride at 85° c. can be calculated. From equation (2) $E^{\circ}_{85°} = +\ 0{\cdot}1716$ v. but

$$E_{85°} = E^{\circ}_{85°} - \frac{RT}{F}\log_e (a_{Cl^-}) \qquad . \quad . \quad . \quad (3)$$

where $T = 358°$ K.

The variations of activities with temperature for solute and solvent are given by equations (4)

$$\frac{\partial \log_e a_1}{\partial T} = -\frac{\overline{L_1}}{RT^2},\ \frac{\partial \log_e a_2}{\partial T} = -\frac{\overline{L_2}}{RT^2} \qquad . \quad . \quad (4)$$

where $\overline{L_1}$ and $\overline{L_2}$ are the relative partial molar heat contents of the solute and solvent respectively, a_1 and a_2 being the corresponding activities.

Since, however, the relative partial heat contents are small for dilute solutions, the activities for such solutions can be regarded as independent of temperature. As before, therefore, the concentration of chloride ions may be substituted for (a_{Cl}) in equation (3), without introducing appreciable error. This leads to the value − 0·380 v., for $E_{85°}$, the potential at 85° c. of the Ag/AgCl electrode in the solution containing 41 p.p.m. chloride. From such values the electrode potentials on the hydrogen scale of the corroding metal specimens being examined can be calculated directly since no junction potentials were involved.

The behaviour of the Ag/AgCl electrode in N. KCl solution has also been considered. The mean activity coefficient for KCl in N. solution at 20° c. is given by Harned [5] as 0·604. Using this value and substituting in equation (1) it is found that the potential of an Ag/AgCl electrode in N. KCl at 20° c. should be + 0·238 v. on the hydrogen scale. This value

[3] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350.
[4] *Ibid.*, 1933, **55**, 2179.
[5] Harned, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Co., 1943), p. 558.

has been confirmed by measurement of Ag/AgCl in N. KCl at 20° c. against N. calomel (in which cell there is no junction potential). The value obtained was $-$ 0·046 v., i.e. $+$ 0·236 v. on the hydrogen scale.

In order to calculate the potential of the Ag/AgCl electrode in N. KCl at 85° c. equations (2) and (3) are used. In this case, however, since the solutions are appreciably concentrated, it is necessary to take into account the variation of activity coefficient with temperature. This is done by means of equation (4). From values given by Harned,[8] $\bar{L}$, the relative partial molar heat content for N. KCl at 25° c. is $-$ 283 cal./mol. Using this value, and 0·606 for the activity coefficient for N. KCl at 25° c., the value obtained for the activity coefficient at 85° c. is 0·655. Substituting this value in equation (3), it is found that the potential of the Ag/AgCl electrode at 85° C., is $+$ 0·186 v. on the hydrogen scale.

(3) Comparison of Potential Measurements made at Different Temperatures.—An attempt was made to find a basis for direct comparison of potential measurements made at different temperatures (i.e. to eliminate effects of a temperature coefficient of the hydrogen electrode, if any exists), by measurements of the E.M.F.'s of cells of the type:

$$\underset{20°\text{ c.}}{\text{Ag/AgCl/MCl}(m)}//\underset{T\,°\text{c.}}{\text{MCl}(m)\text{/AgCl/Ag}} \qquad . \quad . \quad . \quad (1)$$

as T varied between 20° and 85° c.

A summary of the results obtained for a temperature difference of 65° c. for various electrolytes at various concentration is given in Table I below. In each case the hot end of the cell was positive. Also given in Table I are the differences between electrodes at 20° and 85° c. respectively, calculated on the basis of Harned and Ehlers' temperature coefficient for $E°_{Ag/AgCl}$ and taking into account the variations of activity coefficients with concentration and temperature. These values are those corresponding to the E.M.F.'s of cells of the type:

Ag/AgCl	H^+ ($a = 1$) Cl^-(m) other ions for electro- neutrality 20° c.	H_2 Pt——	——H_2 Pt	H^+ ($a = 1$) Cl^-(m) other ions for electro- neutrality T °c.	AgCl/Ag

From these calculated values the hot electrode should be more negative in all cases. The discrepancies between the values obtained from cells (1) and (2) for various electrolytes and concentrations for a 65° c. temperature difference are given in Table I. It is interesting that except for HCl the discrepancy is practically constant at about 0·065 v.

TABLE I

COMPARISON OF E.M.F.'S OF CELLS (1) AND (2) FOR THE TEMPERATURE DIFFERENCE BETWEEN 20° C. AND 85° C.

Electrolyte.	E.M.F. of cell (1) ($\Delta T = 65°$ c.) v.	Calculated E.M.F. of cell (2) ($\Delta T = 65°$ c.) v.	Discrepancy ($\Delta T = 65°$ c.) v.
N. KCl	0·014	$-$ 0·052	0·066
0·0115 N. KCl	0·050	$-$ 0·016	0·066
0·00115 N. KCl	0·037	$-$ 0·030	0·067
0·0875 N. HCl	0	$-$ 0·024	0·024
0·000875 N. HCl	0·023	$-$ 0·015	0·038
N. NaCl	0·014	$-$ 0·051	0·065
0·001 N. NaCl	0·045	$-$ 0·016	0·061

[8] Harned, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Co., 1943), p. 559.

This discrepancy is made up of several factors. Transport occurs in cell (1) but not in cell (2) and the E.M.F.'s should therefore be different by a factor involving the transport numbers of the ions. There is a junction potential in cell (1), and also various thermo-effects in the conductors since the 2 electrodes are at different temperatures. Finally, the discrepancy includes effects due to any temperature coefficient of the hydrogen electrode. Before any estimate of the latter quantity can be made it is necessary to eliminate or estimate all the other effects.

It is likely that thermoelectric effects will be small. Measurements have been made with the usual type of Ag/AgCl electrodes (i.e. Ag on Pt with copper wire connections) and also with electrodes made directly on silver wires, in which case all connecting wires to the measuring instrument (which was at room temperature) were of silver. No appreciable difference was found. The only thermoelectric effect in the second arrangement is that due to the Thomson effect, caused by the drop in temperature along the silver wire. For a 65° C. temperature difference this is not likely to account for any appreciable part of the observed discrepancy.

It is not certain that thermodynamic considerations can be applied to cells of type (1). There appears to be no strong reason why this should not be so, however, since thermodynamics are successfully applied to analogous cells where there is a concentration difference in the two halves instead of a temperature difference. If thermodynamic principles can be applied, it should be possible to make some estimate of the junction potentials involved, at least in the dilute solutions. This would involve an accurate knowledge of the transport numbers of the electrolytes involved, and of their change with temperature. It is possible that the physical form of the liquid junction might affect the value of the junction potential, but this does not appear likely since experiments with cells in which the type of junction was varied, have not given different results for the E.M.F.'s of cell (1).

If the effects described could be calculated with certainty it would be possible to deduce from the values in Table I whether or not a temperature coefficient of the hydrogen electrode exists, and if so, what its magnitude is. On the other hand, careful examination of the thermodynamics involved might show that no information of any value could be derived from such considerations and that there is no possibility of referring electrode potentials to any standard other than that of the hydrogen electrode at the temperature of measurement.

It is felt that this is a theoretical problem the solution of which would help to clarify the position arising when corrosion studies involving potential measurements at different temperatures are made, and discussion of the points raised is therefore invited. The problem of comparison of electrode potential at different temperatures from the point of view of obtaining information about film characteristics, etc., will probably prove to be a complex one, but it is felt that an essential preliminary step is to remove doubt about any possible effect of a temperature coefficient of the hydrogen electrode, if this is possible.

The author wishes to thank Mr. R. P. Bell, F.R.S., for advice and his colleague Mr. H. J. V. Tyrrell, for much helpful discussion.

Summary.

The Ag/AgCl electrode is suitable for use in corrosion work at temperatures up to at least 85° C. and in dilute solutions containing as little as 10 p.p.m. chloride.

Attention is drawn to the desirability in corrosion studies of being able to compare directly potentials measured at different temperatures. Some discussion is given of the basis on which such comparisons may be possible

and of the significance of measurements of the E.M.F.'s of cells with transport with the electrodes at different temperatures, particularly with a view to deciding whether or not the potential of the hydrogen electrode varies with temperature.

Résumé.

L'électrode Ag/AgCl convient pour des études de corrosion, à des températures allant au moins jusqu'à 85° c. et dans des solutions diluées jusqu'au 1/100.000 ème en chlorure.

Il serait souhaitable, pour de telles études, que les potentiels mesurés à différentes températures puissent être comparés directement. Les bases d'un tel mode de comparaison sont discutées, ainsi que le sens que l'on doit attribuer aux mesures des f.é.m. de cellules avec transport dont les électrodes sont à des températures différentes. Cette discussion vise particulièrement à déterminer si le potentiel de l'électrode à hydrogène varie ou non avec la température.

Zusammenfassung.

Die Ag AgCl Elektrode ist für Verwendung in Korrosionsstudien geeignet, u.zw. bei Temperaturen bis mindestens 85° c. und in Lösungen, die nur 10 Teile Chlorid pro Million enthalten. Es wird darauf hingewiesen, dass es in Korrosionsstudien wünschenswert ist, Potentiale, die bei verschiedenen Temperaturen gemessen wurden, direkt vergleichen zu können. Die theoretische Basis eines derartigen Vergleichs und die Bedeutung der elektromotorischen Kräfte von Ketten, in denen die Elektroden an verschiedenen Temperaturen gehalten werden, werden besprochen, mit besonderem Hinweis auf die Entscheidung der Frage, ob das Potential der Wasserstoffelektrode von der Temperatur unabhängig ist.

British Non-Ferrous Metals Research Association,
London.

(b) GENERAL DISCUSSION.*

Dr. J. N. Agar (*Cambridge*) said: I should like to ask Dr. Førland if he can give any estimate of the amount of peroxide formed during electrolysis, to which he referred in introducing his paper. In some work carried out a few years ago on the deposition of oxygen from molten NaOH [1] we were unable to detect peroxides in the electrolyte, but the analysis was carried out some time after switching off the current and after allowing the melt to solidify; the technique was thus different from that used by Flood and Førland.

Dr. T. Forland (*Trondheim*) (*communicated*): Melts of the systems containing phosphate and oxide were tested for peroxide. The tests were carried out in the following way.

A weighing bottle was half-filled with an acid solution of KI and starch. Samples of the melt (some taken out when the cell was in operation and some taken out when the current had been cut off for some minutes) were powdered and put into the bottle; the powder slowly went into solution. After some minutes the solution always became blue. When, however, the samples were taken out when the cell was in operation, the blue colour always started in a layer at the bottom of the bottle, and the solution above was quite clear. In those cases the melt was assumed to contain peroxide.

* On the three preceding papers.

[1] Agar and Bowden, *Proc. Roy. Soc., A*, 1939, 169, 206.

Dr. F. Wormwell (*Teddington*) said: I should like to endorse Mr. Gilbert's remarks on the desirability of being able to compare potential measurements carried out at different temperatures. This would greatly facilitate the interpretation of potential measurements on corroding specimens.

It is gratifying to learn that the silver-silver chloride electrode can be used satisfactorily in natural waters of low chloride content. Is the electrode suitable for prolonged use in natural or artificial sea-waters? Apart from the use of a reference electrode for potential measurements, Miss Brasher and I are interested in measuring the electrical resistance and capacity (with alternating current) of metals covered with protective coatings. Is the silver-silver chloride electrode likely to be suitable as a reference electrode in such work, and in particular is there any information on its capacity?

Dr. T. P. Hoar (*Cambridge*) said: I can confirm that the silver-silver chloride electrode is useful in quite dilute chloride solutions; I have used it for the rapid estimation of traces of chloride ion in emulsions, with results agreeing well with chemical determinations. It may also be of interest to observe that Dr. Thornhill and I, in some work to be reported shortly, found that silver-silver chloride electrodes function reasonably well in sea-water, though they sometimes become unstable through adsorption of impurities, probably organic in nature. Their potential is unaffected by traces of bromide, iodide or sulphide until they have been in contact with sufficient electrolyte to convert almost the whole of the silver chloride into the less soluble silver bromide, iodide or sulphide.

Dr. J. T. Barker (*Flint*) (*communicated*): A definite but conditional answer in the affirmative can be given to Mr. Gilbert's query as to whether electrode potentials in different electrolytes and at different temperatures can be accurately compared. The first condition is that the electrode under test must be compared with the selected standard half-cell by a strictly open-circuit method. Any P.D. in a conducting system must of necessity give rise to, or be associated with, a flow of electricity, unless, as a special case, this P.D. goes along with bound charges, as in the case of a double layer. Miscible electrolytes, even at different temperatures, will not in general give rise to double layers where they meet. Hence on open circuit, when there is no flow of electricity, there can be no P.D. at such liquid junctions. A second condition then is the absence of a double layer there. Instruments, even very sensitive ones, which definitely require small currents for their operation, will not do since at the liquid junction the small current will invoke some P.D. The open-circuit method is moreover well suited to the measurement of the electrode potential of corroded samples, which ought not to be exposed to alteration by electrolytic action.

Prof. A. R. Ubbelohde (*Belfast*) said: The paper by Pearson and Waddington raises a number of problems of great interest for the chemistry of close-packed ionic systems, i.e. for crystal chemistry in the wider sense.

(*a*) It would be interesting to know what is the condition of dissolved Al_2O_3 in molten cryolite. The sublimation energy of this crystal is very high and the comparatively large solubility at around 1000° is probably much above the "ideal" solubility of molecular Al_2O_3.

It would be useful in this connection to know the temperature coefficient of the solubility of Al_2O_3 in molten cryolite, so as to evaluate the heat of solution. A low heat of solution would indicate some kind of ionic dissociation, rather than undissociated Al_2O_3. It may be pointed out that if Al_2O_3 dissociates into ions in the melt, for example,

$$Al_2O_3 \rightleftharpoons Al^{+++} + AlO_3'''$$

this need not make a large difference to the conductivity since it may be anticipated that the mobility of such highly charged ions will be very considerably reduced by the drag of ions of opposite sign. In fact we

might anticipate that in an *ionic melt* the mobility of singly-charged ions such as Na^- will be responsible for carrying most of the current. Any experimental information on this point is of considerable interest in connection with the conduction of electricity in ionic melts, which is probably more closely related to the conduction in ionic crystals than to conduction in dilute solutions of electrolytes.

(*b*) The second point of interest relates to the existence of the ion O'' in the melt. This ion is of considerable interest in connection with the formation of oxide films, and other problems in crystal chemistry, and it is important to have definite evidence for or against the transport of current by this ion. One would like to know how far there may be evidence for its existence in the case of oxides dissolved in other molten fluorites, even if it does not contribute to electric transport in the case of cryolite.

Dr. J. Waddington (*Kinlochleven*) (*communicated*): In connection with the suggestion made by Prof. Ubbelohde that it would be useful to evaluate the heat of solution of alumina in cryolite from the temperature coefficient of solubility, we would mention that the solubility of alumina increases from 13·5 % at 960° c. to 22 % at 1080° c., indicating a relatively low heat of solution.

The suggestion that the fog may consist of sodium vapour, on which Dr. Gross and Dr. Agar commented, was based on the observation that the amount of fog increased markedly with the sodium fluoride content of the electrolyte and that very little visible fog is obtained with electrolytes near the chiolith composition. From the practical point of view and the operation of the furnace it does not matter whether the fog is assumed to be sodium or aluminium.

The following points not mentioned in the paper might be of interest.

(*a*) It has been observed that the size of the gas bubbles escaping from the carbon anode of the cryolite-alumina cell varies with the alumina content of the electrolyte. With high alumina contents a froth of fine bubbles is obtained, but the bubble size gradually increases as the alumina content falls; the bubbles tend to cling more to the anode, until finally, with depletion of the alumina content of the electrolyte, the "up" effect occurs and a continuous film of gas is obtained on the surface of the anode.

(*b*) Although a good cathode current efficiency is obtained when depositing aluminium on a pool of molten aluminium on the bottom of the cell only very poor efficiencies can be obtained if we attempt to deposit the metal on a vertical graphite or carbon plate. The exact explanation of this is not known but it may be due to the escape of fine, negatively-charged globules of metal from the vertical plate.

Dr. J. O'M. Bockris (*London*) said: The existence of the O^{--} ion is made probable by the high conductance possessed by CaO, FeO, etc., in the molten state.[2]

Dr. P. Gross (*Slough*) said: The paper of Pearson and Waddington refers to the existence of a fog consisting of sodium vapour. Since the activity of sodium due to the reaction, $AlF_3 + Na \rightarrow 3NaF + Al$, is less than 1, is not the existence of sodium vapour of 1 atm. excluded? A higher sodium vapour pressure than is possible from this reaction could be produced by the reaction,[3] $Al + NaF \rightarrow AlF + Na$. For the reaction between liquid aluminium and liquid sodium *chloride* the sodium pressure due to the formation of aluminium trichloride or aluminium monochloride, can be calculated because the thermodynamic magnitudes of the aluminium monochloride are known spectroscopically.[4] At 1000° c. the sodium pressure due to the formation of aluminium trichloride is quite small in

[2] Volarovich and Tolstof, *J. Soc. Glass. Tech.*, 1936, **20**, 54.

[3] B.P. Specification, 582,579.

[4] Bhaduri and Fowler, *Proc., Roy. Soc., A*, 1934, **145**, 321; Miescher, *Helv. Phys. Acta.*, 1935, **8**, 486.

comparison with the sodium pressure due to the formation of aluminium monochloride, which itself is still below 1 mm. mercury.

Dr. J. N. Agar (*Cambridge*) said: The formation of metal fogs is of very common occurrence in fused salt electrolysis; Pearson and Waddington suggest that the fog described by them is sodium vapour, but I think that in certain other cases such fogs must consist of the liquid metal. I should like to ask whether they can give any explanation of the ease with which dispersions of this type are formed, and, in particular, whether there are any relevant data on the interfacial tensions between liquid metals and molten salts.

(In reply to Dr. Pearson and Waddington): The formation of bubbles at electrodes, and the size of bubbles when they leave the surface, has been investigated by Frumkin and his co-workers.[5] The contact angle is an important factor, and this depends on the metal-solution interfacial tension, which in turn is a function of the interfacial potential.

The deposition of mercury on graphite electrodes has been studied by Erdey-Grúz and Volmer.[6]

[5] A review is given by Frumkin in *Actualités Scientifiques et Industrielles*, Fo. 373 (Hermann et Cie., Paris, 1936).
[6] Volmer, *Physik. Z. Soviet Union*, 1933, **4**, 346; Erdey-Grúz and Volmer, *Z. physik. Chem.*, 1931, **157**, 182; Erdey-Grúz and Wick, *ibid.*, 1932, **162**, 63.

THE STANDARD ELECTRODE POTENTIALS OF THE ELEMENTS

By J. O'M. Bockris and J. F. Herringshaw,

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An obvious necessity exists for a survey of the numerical values of the standard electrode potentials. Older collections * are now of limited use, and the scattered nature of the relevant literature makes difficult a rapid re-orientation by a single worker. Indeed, a comprehensive and critical examination of the data can only conveniently be carried out where a comparatively large team of workers specialising in electrochemistry is available, as in this Department, so that a system of independent checking of an examination of the literature can be made.

In the present summary, attention has been concentrated on electrode potentials corresponding to equilibria of the type:

$$M^{z+} + ze \rightleftharpoons M \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$A + ze \rightleftharpoons A^{z-}, \quad . \quad . \quad . \quad . \quad (2)$$

where e is the unit electronic charge and z is a small integer. In a few instances, where no such values are available, standard electrode potentials are given which refer to some other simple reaction involving the given element in a solution of its ions.

All values refer to aqueous solutions at 25° C. The small amount of work relating to non-aqueous solutions is discussed in a recent review by Pleskov.[1]

* See, e.g., Gerke, *Chem. Rev.*, 1924, **1**, 377.

Definitions.—The reversible electrode potential of an element in a solution of its ions at an activity a_i is defined by the expression :

$$e = e_0 + \frac{RT}{zF}\ln a_i \quad . \quad . \quad . \quad . \quad (3)$$

if the element forms positive ions and the relevant equilibrium reaction at the electrode-solution interface is (1); and by the expression

$$e = e_0 - \frac{RT}{zF}\ln a_i \quad . \quad . \quad . \quad . \quad (4)$$

if the element forms negative ions and the relevant reaction is (2).

The term a_i is given by

$$a_i = \gamma_i c_i \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where c_i is the stoichiometric molality of the ion of the electrode material and γ_i is the corresponding stoichiometric activity coefficient of this ion.

Electrode potentials derived from eqn. (1) and (2), have a sign according to the European convention, i.e. when the electrode potential is represented by a positive number on the standard hydrogen scale, the electrode is more positive than the standard hydrogen electrode.

The standard electrode potential is defined by e_0 in (3) and (4), or approximately as " the potential of the electrode in a solution in which its ions have unit activity." In a complete definition it is necessary to state the reaction at the electrode-solution interface to which the given standard electrode potential refers. Because it is not possible to measure unambiguously an absolute metal-solution potential difference, electrode potentials are recorded with reference to the standard reversible hydrogen electrode. The standard reversible electrode potential of hydrogen (for which $a_{H^+} = 1$ and $p_{H_2} = 1$) is taken as zero at all temperatures.

Evaluation of Standard Electrode Potentials.—The following difficulties arise in evaluating standard electrode potentials according to the definition given above.

Single Ion Activities.—Eqn. (3), (4) and (5) involve the activity of a single ionic species, which cannot at present be determined unambiguously by experiment. It is often necessary to make use of mean ion activities of the salt containing ions of the element and this procedure must introduce an approximation so that single electrode potentials measured in this way lack precise significance. Frequently, data are not available for the activity coefficient of the salt over the appropriate concentration range. In such cases an attempt may be made to calculate the relevant activity coefficient from the appropriate theoretical equations of the interionic attraction theory of activity in ionic solutions. These equations are particularly inapplicable for polyvalent ions where they are most needed, and moreover, the salting-out constant of these equations is often unknown.

Densities of the Solutions. Authors express their results with reference to weight or volume concentrations. For a uniform presentation of standard electrode potentials, therefore, it is necessary to know the densities of the appropriate solutions and these are often not available.

The Liquid-Junction Potential. Liquid-junction potentials arise in many determinations of standard electrode potentials and are frequently unsatisfactorily eliminated. Calculations of corrections for this factor from, e.g., the Henderson equation are not satisfactory for results of high precision.

Irreproducibility of Measurements. The large effect of the state of the electrode surface, often stressed as a factor governing the potential associated with an irreversible electrode process, is generally contrasted with the small effect of this factor on reversible electrode potentials. A detailed examination of the literature does not support this contention. Effects of surface characteristics on reversible electrode potentials are probably partly due to the different degrees of mechanical strain in the metal induced by different modes of preparation. Impurities, particularly occluded gases, present in varying quantities, may have a considerable effect on the electrode potential by introducing other reactions at the electrode-solution interface. Lack of complete reversibility of the electrode reaction may also cause irreproducible measurements.

TABLE I.

Electrode Reaction.	e_0 (Volts). ±1 mv. A.	±1 cv. B.	±? v. C.	Notes.	Ref.
$\frac{1}{2}N_2 + e \rightleftharpoons N_3^-$	—	—	−3·2	Calc. Exptl. values irreproducible; electrode reaction irreversible (15, 90)	13, 89
$Li^+ + e \rightleftharpoons Li$	—	−3·01	—	Exptl. and calc. values somewhat discrepant. Mean value given; see also 33	2, 3
$Rb^+ + e \rightleftharpoons Rb$	—	−2·98	—	Fair agreement of independent determinations; but see 33	2, 5 (calc.); 3 (exptl.)
$Cs^+ + e \rightleftharpoons Cs$	—	−2·92	—	Calc. and exptl. values agree; but see also 2, 33	34 (calc.) 35 (exptl.)
$K^+ + e \rightleftharpoons K$	—	−2·92	—	Good concordance of results; but see 33	2, 5 (calc.) 3, 36 (exptl.)
$Ba^{2+} + 2e \rightleftharpoons Ba$	—	−2·92	—	Calc. value; exptl. value −2·15 from fused salts measurement (33)	2, 37, 38
$Sr^{2+} + 2e \rightleftharpoons Sr$	—	−2·89	—	Calc. value; exptl. value −2·86 (38), but see 33	2, 37, 38
$Ca^{2+} + 2e \rightleftharpoons Ca$	—	−2·84	—	Calc. value; exptl. values −1·90 (33) to −2·76 (39)	2, 37
$Na^+ + e \rightleftharpoons Na$	−2·713	—	—	—	2, 3, 4, 5, 6
$La^{3+} + 3e \rightleftharpoons La$	—	—	−2·4	Calc. and exptl. values very discrepant; see see also (91)	2
$Mg^{2+} + 2e \rightleftharpoons Mg$	—	−2·38	—	See also 2, 34, 38, 41 for other calc. values; see also 42 and 43 for discrepant exptl. values	40
$Th^{4+} + 4e \rightleftharpoons Th$	—	—	−2·1	Calc. value	2
$Ti^{2+} + 2e \rightleftharpoons Ti$	—	—	−1·75	Calc. value	2
$HfO^{2+}+2H^+ + 4e \rightleftharpoons Hf+H_2O$	—	—	−1·7	Calc. value	2
$Be^{2+} + 2e \rightleftharpoons Be$	—	−1·70	—	Calc. value; exptl. values, −1·1 to −1·9 (84, 85)	2, 83
$Al^{3+} + 3e \rightleftharpoons Al$	—	−1·66	—	Mean of two calc. values; exptl. values very doubtful, see 45 and 46	34, 44
$ZrO^{2+}+2H^++4e \rightleftharpoons Zr+H_2O$	—	—	−1·5	Calc. values	2
$V^{2+} + 2e \rightleftharpoons V$	—	—	−1·5	Calc. values (±0·3)	2
$WO_4^{2-}+4H_2O+6e \rightleftharpoons 8OH^-+W$	—	—	−1·1	Calc. from est. value of entropy of WO_4^{2-}	2
$Mn^{2+} + 2e \rightleftharpoons Mn$	—	—	−1·05	Calc. values	2, 92, 93
$Te + 2e \rightleftharpoons Te^{2-}$	—	—	−0·92	Calc. value; second dissociation const. of H_2Te not available; exptl. value, −0·84 (94)	13, 75
$UO_2^{2+}+4H^++6e \rightleftharpoons U+2O_2H$	—	—	−0·82	Calc. entropy of ion uncertain	2
$Se + 2e \rightleftharpoons Se^{2-}$	—	−0·78	—	Calc. values (independent data)	13, 47

TABLE I (*continued*).

Electrode Reaction.	ϵ_0 (Volts). ± 1 mv. A.	± 1 ev. B.	± ? v. C.	Notes.	Ref.
$Zn^{2+} + 2e \rightleftharpoons Zn$	−0·763	—	—	—	7, 8, 9, 10, 11
$H_3BO_3+3H^++3e \rightleftharpoons 3H_2O+B$	—	—	−0·73	Calc. value	2
$Cr^{3+} + 3e \rightleftharpoons Cr$	—	—	−0·71	Calc. value	2
$SbO_2^-+2H_2O+3e \rightleftharpoons Sb+4OH^-$	—	−0·67	—	Calc. and exptl. values	76, 77
$Ga^{3+} + 3e \rightleftharpoons Ga$	—	−0·52	—	Exptl. value	48
$S + 2e \rightleftharpoons S^{2-}$	—	−0·51	—	Calc. values based on thermal data for H_2S; agree with Ag | Ag_2S | H_2S electrode measurements; see also 51, 52	49, 50
$Fe^{2+} + 2e \rightleftharpoons Fe$	—	−0·44	—	Exptl. values	13, 53, 54, 55
$Cd^{2+} + 2e \rightleftharpoons Cd$	−0·402	—	—	—	5, 11, 12
$In^{3+} + 3e \rightleftharpoons In$	—	−0·34	—	Exptl. values	56, 57
$Tl^+ + e \rightleftharpoons Tl$	−0·335	—	—	—	13, 14, 15
$Co^{2+} + 2e \rightleftharpoons Co$	—	−0·27	—	Exptl. values	58, 59, 60
$Ni^{2+} + 2e \rightleftharpoons Ni$	—	−0·23	—	See also 14, 63, for data in presence of H_2	61, 62
$Mo^{3+} + 3e \rightleftharpoons Mo$	—	—	−0·2	Calc., mainly from estimated data	2
$Sn^{2+} + 2e \rightleftharpoons Sn$	−0·140	—	—	—	13 (corrected by the value of ϵ_0 for Pb given here), 16
$Pb^{2+} + 2e \rightleftharpoons Pb$	−0·126	—	—	—	16, 17 18, 19, 20, 21
$D^+ + e \rightleftharpoons \frac{1}{2}D_2$	—	−0·003	—	Exptl. value	65
$HAsO_2+3H^++3e \rightleftharpoons As+2H_2O$	—	0·25	—	Calc. from exptl. E.M.F. values of reaction $As_2O_3+3H_2 \rightleftharpoons 2As+3H_2O$	2
$BiO^+ + 2H^+ + 3e \rightleftharpoons Bi + H_2O$	—	0·32	—	Exptl. values	66, 67
$Cu^{2+} + 2e \rightleftharpoons Cu$	—	0·34	—	Exptl. values	68, 69, 70, 71, 72, 73
$\frac{1}{2}O_2 + H_2O + 2e \rightleftharpoons 2OH^-$	0·401	—	—	Calc. values	78, 79, 80, 81, 82
$Cu^+ + e \rightleftharpoons Cu$	—	0·52	—	Calc. from equil., $Cu + Cu^{2+} \rightleftharpoons 2Cu^+$	116
$I_2 + 2e \rightleftharpoons 2I^-$	0·536	—	—	—	13, 22, 23
$Te^{4+} + 4e \rightleftharpoons Te$	—	0·56	—	Calc. and exptl. values	74, 75
$Po^{3+} + 3e \rightleftharpoons Po$	—	—	0·56	Various exptl. data discrepant	95, 96
$Rh^{2+} + 2e \rightleftharpoons Rh$	—	—	0·6	Calc. value; no knowledge of free energies of solution of oxides	2
$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	0·798	—	—	—	13, 24
$Ag^+ + e \rightleftharpoons Ag$	0·799	—	—	—	13, 25, 26
$Pd^{2+} + 2e \rightleftharpoons Pd$	—	—	0·83	Exptl. value; see also 97	99
$Ir^{3+} + 3e \rightleftharpoons Ir$	—	—	1·0	Calc. value	2
$Br_2(l) + 2e \rightleftharpoons 2Br^-$	1·066	—	—	—	27, 28
$Pt^{2+} + 2e \rightleftharpoons Pt$	—	—	1·2	Calc. from data on $Pt(OH)_2+2H^+ + 2e \rightleftharpoons Pt + 2H_2O$	2
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	1·358	—	—	—	13, 29, 30, 31, 32
$Au^{3+} + 3e \rightleftharpoons Au$	—	—	1·42	Calc. from E.M.F. data (100, 101)	2
$Au^+ + e \rightleftharpoons Au$	—	—	1·7	Calc. assuming the solubility of AuI to be analogous to that of CuI and AgI	2
$F_2 + 2e \rightleftharpoons 2F^-$	—	2·85	—	Calc., calc. and exptl. values discrepant (81, 88)	86

IRREVERSIBILITY OF ELECTRODE REACTION. Incomplete reversibility of the electrode processes at the metal-solution interface during the determination of electrode potential vitiate the applicability of the thermodynamic expressions. Evidence of irreversibility of electrode processes is hence of great importance. This may be summarised :

(i) fluctuations occur in the electromotive force of the relevant cell ;

(ii) apparently identical electrodes under the same conditions in the same solution do not exhibit the same potentials ;

(iii) changes of electromotive force of the cell occur on agitation of the solution ;

(iv) the variation of the electrode potential with changing values of a_i does not conform with values given by (3) and (4) ;

(v) a rapid return to the potential of the resting electrode does not occur after passage of current through the electrode for a short time.

SOLVATION ENERGIES. Finally, discrepancies arising in certain calculated values of standard electrode potentials arise partly from lack of knowledge concerning the distribution of the solvation energy between the positive and negative ions of the relevant salt.

Arrangement of Values of Standard Electrode Potentials.—The agreement between the results of independent work is relatively poor, except for some of the softer metals where concordance of about 1 mv. is found among several independent determinations. For many elements, much larger discrepancies occur due partly to the difficulties of determination described above, but more frequently to lack of relevant data which makes for the accurate evaluation of e_0. On this account, the present collection distinguishes three classes of values.

In Table I, Column A refers to those elements for which there are apparently reliable independent data, concordant to within about 1 mv., which lead to an evaluation of the standard electrode potential.

Column B refers to those elements for which insufficiently reliable data are available for an accurate evaluation of the standard electrode potential. In this case, the most accurate results in the literature concerning the standard electrode potential are given with explanatory notes. The concordance between independent determinations is of the order of 1 cv.

Column C refers to those electrode potentials the values of which are of an extremely provisional nature.

Table II refers to the standard electrode potentials of some well-known half-cells, the values given being of an accuracy comparable with that of the values in Table A.

TABLE II.—STANDARD POTENTIALS OF SOME WELL-KNOWN HALF-CELLS.

Electrode.	e_0 (Volt).	Ref.
$Pb(Hg)-PbSO_4 . SO_4''$	−0·351	114, 115
$Ag-AgI . I'$	−0·152	102
$Ag-AgBr . Br'$	0·071	98, 103, 104, 105, 106
$Hg-HgO . OH'$	0·098	107, 108
$Hg-Hg_2Br_2 . Br'$	0·140	109
$Ag-AgCl . Cl'$	0·222	98, 110, 111
$Hg-Hg_2Cl_2 . Cl'$	0·268	112, 113
$Hg-Hg_2SO_4 . SO_4''$	0·615	98
$Pt-PbO_2 . PbSO_4 . SO_4''$	1·685	115

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Contents

AUTHOR INDEX*

* Page numbers in Clarendon type indicate papers submitted for discussion.

Discussions of the Faraday Society

No. 2, 1947

THE LABILE MOLECULE

GURNEY AND JACKSON
LONDON: 98 GREAT RUSSELL STREET
EDINBURGH: TWEEDDALE COURT

THE LABILE MOLECULE

A GENERAL DISCUSSION HELD ON

23rd, 24th and 25th SEPTEMBER, 1947.

A GENERAL DISCUSSION on The Labile Molecule was held in the Physical Chemistry Laboratory at the University of Oxford (by kind permission of Prof. C. N. Hinshelwood, F.R.S.) on the 23rd, 24th and 25th September, 1947. The President, Prof. W. E. Garner, C.B.E., F.R.S., was in the Chair and about 250 members and visitors were present.

Among the distinguished overseas members and guests welcomed by the President, were the following :—

> Prof. T. Alfrey (Brooklyn), Dr. and Madame Daudel (Paris), Dr. P. Goldfinger (Nancy), Mr. P. ten Have (Delft), Prof. and Madame J. C. Jungers (Louvain), Mlle. J. Lacau (Paris), Dr. M. Magat (Paris), Dr. I. Mallah (Paris), Dr. F. Mayo (Passaic, N.J.), Dr. K. Nozaki (Emeryville, Cal.), Prof. C. C. Price (Notre Dame, Ind.), Dr. R. E. Robertson (Ottawa), Dr. P. Rumpf (Paris), Dr. G. Salomon (Delft), Dr. J. van Santen (Eindhoven), Dr. E. W. R. Steacie (Ottawa), Dr. C. E. Sunderlin (U.S.N., London), Dr. A. van Tiggelen (Louvain), Dr. A. V. Tobolsky (Princeton), Dr. J. G. van Veersen (Delft), Dr. C. Walling (Passaic, N.J.), and Dr. K. Wieland (Zurich).

The papers had been issued in Advance Proof; these, and reports of the Discussion, are published in the present volume; they have been arranged under the following headings :—

I. Theoretical.

II. Gas Phase.

III. Liquid Phase:
- A. Electron-transfer Reactions.
- B. Hydrocarbons in Solution.
- C. Oxidation-reduction Reactions.
- D. Experimental Technique.

IV. Polymerisations:
- A. Reactions of Radicals and Monomers:
  (a) Initiation; (b) Propagation.
- B. Chain transfer and Inhibition.
- C. Degradation.

THE LABILE MOLECULE

INTRODUCTORY ADDRESS.

By H. W. Melville.

It is usually the custom of the Faraday Society to select a limited topic for its discussions in order that a developing subject may be subjected to critical discussion and appraisal. On this occasion the same general point of view has been taken but, in addition, an attempt has been made to achieve a synthesis of a number of branches of chemistry which had hitherto been rather far apart and whose development now has reached a stage at which they may profitably be discussed together. It happens, therefore, that the field of chemical kinetics acts as a kind of binding force between the extremes of the application of wave-mechanical calculations to the energies of free radicals and of the investigation of reactivity in comparatively complex organic reactions; the kind of bond that welds the subject into a coherent whole is the behaviour of free radicals. Many years ago the Society held a discussion on free radicals at a time when the existence of simple free radicals in the gas phase had been established and some of the implications of gas-phase free-radical chemistry revealed. Much has happened since that date and it was consequently felt that a new stage had now been reached which merited discussion, the main emphasis being not so much on the discovery of new radicals but the quantitative formulation of the multiplicity of reactions that such radicals may undergo with other molecules and radicals. As will be seen from the discussion, the quantitative significance becomes paramount because the absolute magnitude of the velocity coefficients determines in the end the observed overall characteristics of the total reaction.

The hitherto separate parts of the discussion have originated in diverse ways and it may therefore be worthwhile to try and show where the threads of the story start so that their eventual intertwining may more readily be appreciated. However, the systematic advances in chemical kinetics have played the dominant role in developing free-radical chemistry to its present fairly high level of precision. During the early part of the present century the pioneering work of Bodenstein and others on both the thermal and photochemical reactions of the halogens demonstrated that free halogen atoms were certainly the active entities whereby reaction was induced among normal stable molecules. This recognition of their high reactivity then led to further investigation of methods of the production, isolation and of following the reactions of free hydrogen, oxygen and other atoms. In this way a kinetics of free-atom chemistry was rapidly built up alongside the more formal development of chemical kinetics. At about this period one of the main topics of kinetics was to establish a relationship between velocity coefficients and energy of activation no matter the identity of the reacting particles. It proved most convenient to study molecule-molecule interactions, that is to say, reactions in which nothing emerged from the act of chemical transformation that would have any further influence on the system. Although the study of such cases revealed certain important generalisations regarding reactivity, further investigation showed that simple bimolecular interactions were rarely encountered in the ordinary course of events and that as experience grew the importance of chain processes became more and more apparent. Here there came a conflict of viewpoint. While kinetic analysis was sufficiently powerful to specify clearly what collision types comprised the whole reaction it was really impossible except in very simple cases, to identify the nature of the active particles—indeed the idea of "hot" molecules was frequently postulated when free atoms or radicals could not be made to conform to

kinetic requirements. But that state of affairs was more due to a lack of knowledge of the behaviour of radicals than to a desire to invent improbable hypothetical molecular entities as chain carriers. All the extensive work on oxidations, both stable and explosive, and especially the effects associated with surfaces and the presence of inert gas showed very clearly that the chain carriers had a life characteristic of free atoms or radicals and that electronically excited molecules, except special metastable molecules, could not possibly behave in the way required of the kinetics. Generally speaking, therefore, a more exact knowledge of radical chemistry, obtained by new and independent methods, will undoubtedly clear up many matters which have had to be left unsettled since kinetic analysis had reached a limit.

Another line which is complementary to the kinetic approach and one of the independent methods so necessary to support the purely kinetic evidence is the spectral examination of the radical emission in flames. It is known that there is a very close relationship between the kinetics of reactions at the explosion limit and outside it in the stable region, but it is unfortunately by no means certain that the emitting radicals in a flame are necessarily the chain carriers under explosive conditions and also under stable conditions. The difficulty is that under stable conditions, radical concentrations are inevitably so small that detection, even by absorption methods, has not proved so far a practicable proposition. This is a most unfortunate matter because a knowledge of the actual stationary concentration might be obtained if the method were sufficiently sensitive. In fact it is the lack of knowledge about that concentration that certainly holds up progress completely in this field.

It is perhaps curious that the study of oxidation in the liquid phase has lain dormant for such a long interval. The initial work on aldehydes and aqueous sulphite laid the foundations of the theory of thermal chain reactions. Probably the matter was not followed up for the simple reason that matters appeared to be so complex in the gas phase that the additional troubles encountered in working in a condensed system would preclude any significant progress being made. Work in recent years, however, has tended to show that these complications are not so formidable as was once thought to be the case provided certain precautions are taken. The first main difficulty is to choose a system in which the oxidation does not go too far and in which, as far as possible, only a single end product is produced. Here the work of organic chemists has been of especial value for suitable reactions for kinetic study have been isolated as, for example, in the oxidation of hydrocarbons, unsaturated esters, and of polymers such as polyisoprene to hydroperoxides which are sufficiently stable not to decompose further into complicated products. In such cases it would appear that the two essential steps in the reaction are

$$R— + O_2 \rightarrow RO_2—$$
$$RO_2 + RH \rightarrow RO_2H + R—$$

where R— is a radical produced by the radical dehydrogenation of the organic compound undergoing oxidation. Further, it seems that the second is the slower step in the process. What is not quite so well established is how the RO_2— radical disappears—the kinetics in many cases reveal differences which do not lead to an unequivocal answer on this point, but this is a matter which can ultimately be settled by sufficient experiments. But there is not yet any well-defined opinion as to how the radical is generated in the first place although if hydroperoxide accumulates, its thermal or photodecomposition will certainly provide a source of radicals. In photochemical reactions, e.g. with aldehydes and some hydrocarbons, radiation might lead to the fission of the molecule with the production of radicals or it might facilitate primary attack by oxygen itself. Although it is easy conveniently to forget this stage it is absolutely vital for the whole analysis.

The fate of the peroxides is of great importance for it may turn out that their decomposition also proceeds by a chain process independently of, but with a vital influence on, the oxidation itself. The complicated manner in which many of these peroxides decompose makes it difficult in most cases to subject such reactions to a close kinetic study. It is to be hoped that the knowledge gained in the investigation of liquid phase oxidations at low temperatures may have its bearing on gas phase oxidations especially with a view to discovering what kinds of radicals participate and how they are generated and disappear.

The study of oxidation reactions provides another opportunity for learning about the behaviour of radicals towards other molecules. A great variety of substances either strongly inhibit or retard oxidations. If the latter phenomenon occurs, there is a competition between the substance being oxidised and the retarder for the ROO-radical. Consequently it at once becomes possible to get a measure of the relative velocity coefficients for radical-molecule interactions. Furthermore, if some day it becomes practicable to measure the stationary concentration of the radical —and that in principle is possible—the absolute values of the velocity coefficients may then be calculated. The problem still remains of measuring the velocity with which the radical takes up oxygen and although this is probably a very fast reaction it is of importance to devise some method of performing this task.

Maybe the biggest recent development in free-radical chemistry has occurred in the study of ethylenic polymerisation at room temperatures and higher. It has taken some little time to establish quite conclusively that free radicals are the intermediates but there now seems no other possibility. The most convincing evidence comes from the fact that the introduction of radicals in the gas or liquid phase at once leads to polymerisation and that the kinetics of polymerisation are in general similar to those in which peroxides, radiation and heat, are used to start off molecular growth. The nature of the radical is therefore not in doubt. Moreover the variety of effects that can be observed in polymerisation is such that it may turn out that this will become one of the most useful techniques for the study of radical reactions. In polymerisation reactions the fundamental step is the interaction of a radical with a double bond to yield a larger radical, namely $R— — CH_2CHX = R.CH_2.CHX—$. It is only very recently that it has become possible to measure the velocity coefficient of the reaction but it should not be long before a sufficient variety of systems has been investigated to get a general idea of the factors that govern the magnitude of the coefficient. Already by a study of interpolymerisation some light has been thrown on the effect of the nature of X on reactivity. It is, however, quite clear that the magnitude of the coefficient will be a function of the nature of the attached radical as well as the nature of X. While in polymerisation the radical R— will be derived from the monomer itself, it is also of importance to devise methods of measuring the velocity of the interaction of a great variety of radicals with ethylenic compounds. The beginnings of this part of work are recorded in some of the papers presented below. The data here will provide the theoretical worker with the material he needs to see to what extent it is practicable (*a*) to calculate the potential reactivity of radical as a function of its structure and therefore energy content and (*b*) the effect of X on reactivity with the additional interesting correlation of the effect of similar substituents on the effect of reactivity of positions in the benzene ring and similar phenomena. Sufficiently accurate work will enable both the energy and entropy factors to be disentangled and then it becomes of especial importance to see how the size of a polymer radical affects its reactivity. In accordance with expectation such effects are not large if the radical is big enough but so far there is no evidence about the behaviour of velocity coefficients in the initial stages of growth of the polymer.

Just as oxidation reactions are retarded or sometimes completely suppressed, so may polymerisation reactions be similarly affected but not necessarily by the same agents. The same general mechanism is, however, involved because a radical has to be destroyed or inactivated. Except if the inhibitor is a free radical itself and cases of this are known, e.g. Ph_2N, $Ph_2C . CN$ in the polymerisation of acryl acetate (McLaren, unpublished experiments) a radical cannot be destroyed and therefore it must be presumed that the inhibition process involves the production of another kind of radical which is so unreactive that it cannot take any further essential part in the reaction. Normally this would occur by the removal of an atom from the inhibitor molecule, the radical so produced being incapable of continuing reaction. On the other hand, if the inhibitor molecule is unsaturated it may add on to the polymer chain, the new radical being incapable of adding on further molecules of monomer. There must, however, be a continuous gradation in the reactivity of radicals and the clear-cut distinction made above will only hold in extreme cases. If, for example, inhibition involves bodily removal of an atom and the resultant radical does react then the phenomenon of transfer appears, the result not only being a reduction in the molecular weight of the polymer but also a diminution in rate. In the case of the unsaturated inhibitor, copolymerisation will occur if the radical does have a tendency to react with monomer. Again going to the other extreme the retarder may completely suppress reaction. The general mechanism of such inhibition must mean in the case of unsaturated molecule the rapid addition of two radicals before the chain process has had time to operate, and with saturated molecules, the rapid interaction of the radical produced from the inhibitor with chain starting radicals. In this field much more exact *chemical* data are required regarding the nature of the products for it is only in this way that the chemistry, apart from the kinetics, of these reactions can be fully worked out.

One of the biggest barriers in quantitative free-radical chemistry is the precise determination of the manner in which radicals disappear by mutual interaction. Kinetically it is usually simple to determine whether or not this process operates for a rate dependency involving the square root catalyst concentration or light intensity usually provides the clue. There is, however, practically no information about how often such processes occur in the gas or liquid phases. It is not even known with certainty whether disproportionation or combination occurs, whether energy of activation is required and what is the magnitude of the entropy term. In free-atom reactions at any rate in the gas phase, matters are relatively simple—three-body or wall combination—but with complex radicals it is most unlikely that the simple generalisation applicable to atoms will ever hold even with small hydrocarbon radicals. It is fortunate that a number of methods are available for determining the rate of *production* of radicals—but each needs to be used with a good deal of caution. The present methods depend usually on the measurement of kinetic chain length. This is most readily accomplished by measuring the rate of consumption of retarder in a well-retarded reaction—or sometimes by measuring the length of an induction period during which a strong inhibitor is being removed. The quantum yield in a photochemical reaction might likewise be used but the difficulty here is being certain that each quantum of absorbed radiation starts off a chain. Experience shows that such an assumption cannot necessarily be made. In polymerisations fortunately there is another method because if there is no transfer the number average chain length of the polymer will give the kinetic chain length. Again there may be minor complications because of the uncertainty regarding disproportionation or combination of the radicals. Similarly the rate of decomposition of peroxides, azo compounds, etc., may give the rate of interaction of radicals with monomer or oxygen in an oxidation reaction but once again special attention has to be paid to

the possibility that each radical may not necessarily start off a chain, especially if that radical is not too reactive.

The other important quantity is the concentration of radicals attained during the stationary state condition or better still under any conditions. It is true that a number of methods exists for the determination of the concentration of radicals, e.g. by measurement of paramagnetism, optical properties, etc. These methods unfortunately only are of use if the concentration of radicals is high, e.g. 10^{-5} moles/l., which concentrations may be reached with radicals of the triphenyl methyl type. The important fact is that such radicals are in general so unreactive that they are of little interest in connection with oxidation or polymerisation processes. In these latter reactions the concentrations are more likely to be in the range 10^{-7}-10^{-10} moles/l. The direct physical methods of measurement simply cannot reach these magnitudes, far less make accurate measurements in a limited period of time, e.g. 10^{-3} sec. The problem may, however, be solved by determining the average life of the radical for, with a knowledge of the rate of production of radicals, this will give an accurate measure of the concentration. For this purpose only the photochemical method of starting can be used since it is so readily controllable. If intermittent radiation is employed the rate of reaction is a function of the period of intermittency provided the radicals disappear two at a time. Mechanical methods of giving intermittent illumination are easy to use down to 10^{-3} sec. In some polymerisation reactions the life of the radicals is sometimes so long that it is merely necessary to observe the rate of decrease of reaction velocity with time, after the light is switched off, to compute the life of the radicals. Although this method might appear to be restricted in its scope because of the fact that radiation may not in fact initiate reaction, it is usually possible to add a photosensitiser and often the most convenient sensitiser for oxidation and polymerisation are peroxides, which seem to act in the same way whether their decomposition is brought about thermally or by radiation. Much of the work done on the photochemistry of simple organic compounds, for example ketones, is particularly relevant here since a radical mechanism for decomposition is in most cases a well-established fact. There is still need for much progress to be made here if the quantitative aspect of the subject is to advance. On the other hand there is sometimes a natural barrier. As in all kinetic work it is desirable to choose those reactions which kinetically are simplest so that analysis does not merely indicate the general scheme but enables one to compute coefficients accurately. This highly desirable state of affairs is unfortunately unobtainable with some systems but the range of conditions under which reactions may now be measured is so great that the kinetic difficulties ought to be capable of being surmounted.

The aims of the present discussion can therefore be set down very simply. These are to study reactions in the gas and liquid phases whose mechanism is, by well-known methods, known to occur through the intermediary of free radicals. The rate of radical production, the mode of disappearance both naturally and in presence of added substances must be measured by quantitative methods. Such studies will therefore build up a chemistry of free radicals which may be used in two ways. It will enable us more precisely to predict and control the course of reactions not yet studied; it will provide data for the foundation of theory of radical reactivity. There is, however, no need to wait till the experimentalist has established a body of data. Much of the present data is urgently in need of interpretation on well-defined theoretical principles.

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I.—THEORETICAL.

INTRODUCTORY SURVEY—THE THEORY OF FREE RADICALS.

By C. A. Coulson.

Received 30*th October*, 1947.

The papers which are presented in this theoretical section of the Discussion show that although some considerable progress has been achieved in the 15 years during which attempts have been made to apply wave mechanics to a study of the properties and reactivity of free radicals, there is nevertheless only a restricted field in which reliable quantitative results have been obtained. This is not surprising when it is realised how many and diverse are the factors which govern the ultimate reactivity of any compound.

The first paper, by myself (p. 91), is a review of such theoretical work as has already been published on the structure and reactivity of free radicals. In view of its nature it does not require any further comment here, except to draw attention to the table just before the end, where the nomenclature used by different workers is put together. This should be a convenience to those who are not familiar with the various techniques, and it should help to make more clear just what is meant by some of the other speakers in this part of the Discussion.

The next paper, by Walsh (p. 18), stands alone, but it comes in natural sequence to a good deal of theoretical work in the last few years. For it is now recognised that carbon forms bonds in which the individual character of the atomic *s* and *p* orbits is lost, being merged in a mixed, or hybridised, type of orbit. It is this hybridisation that, for example, most distinguishes aliphatic and aromatic carbon. Even in one given molecule, if the groups attached to the carbon are not equivalent, the bonds will themselves not be equivalent either. There is, in fact, a continuous interplay between the proportions of *s* and *p* in each bond, maintaining, of course, constant grand totals of *s* and *p*. Now the space configuration of the bonds around the central atom is regulated by the amounts of *s* and *p* in the various bonds, so we have a link between the electronegativity of the attached groups and the shape of the molecule. Walsh shows that this relation leads one to believe that the methylene radical CH_2 has an angle in the region of 140° or 145° (as suggested by Herzberg). This makes the carbon atom in CH_2 rather like an ethylenic carbon, and has considerable bearing on the energies of removal of successive hydrogens from CH_4.

The next two papers, by Daudel (p. 25) and Pullman (p. 26), cover somewhat similar ground. Dr. Daudel discusses the polyene chain radicals with an odd number of carbons, using the valence bond, or resonance, technique of Pauling. He calculates the bond orders and the free valences, getting excellent agreement with those previously obtained by use of the alternative molecular-orbital treatment. In particular the alternating double-single-double bond character of the even-numbered chains (e.g. butadiene =—=) is much more smoothed out in the odd chains; but the free valences are greater than in the even chains, and especially great at the ends. Madame Pullman extends Daudel's work by including more canonical structures in each radical; and she also applies her technique to conjugated free radicals. For the particular cases of phenylmethyl and biphenylmethyl she shows that the free valence is largely, though by

no means entirely, on the methyl carbon; but as the number of phenyl or biphenyl groups around the central carbon is increased the free valence on this carbon atom steadily diminishes.

The next group consists of the papers by Szwarc, by Coulson, Craig, Maccoll and Pullman, and by Dewar. Szwarc (p. 39), gives us two papers, though in effect he discusses three somewhat related topics. In the first, which is as much experimental as theoretical, he shows that the resonance energy of the benzyl radical is larger than anticipated, and gives some reasons why we might argue that the central single bond in dibenzyl was stronger than a normal ethane-type bond. Then he goes on to discuss triphenyl methyl. If the replacement of one hydrogen of CH_3 by a phenyl leads to considerable resonance energy, we might have expected, at first, that replacement of all three to give triphenyl methyl would have led to a very large resonance energy. In fact it is not so, and the resonance energy may not be much different from that of benzyl, on account of steric hindrance preventing the three phenyl rings from being coplanar. In his second paper he shows that the meri-quinone molecule (*p*-quinodimethane) obtained by replacing the two oxygens of *p*-quinone by CH_2 groups, is stable in the gas phase, but in the liquid phase it is very labile and rapidly polymerises.

The discussion of *p*-quinodimethane is also taken up by Coulson, Craig, Maccoll and Madame Pullman (p. 36). Both the molecular-orbital and the valence-bond methods are applied in the conventional manner to calculate the resonance energies, free valences and bond orders both in the ground state (which is a singlet) and in the excited (triplet) state. This latter is the genuine di-radical configuration, but, rather surprisingly, the free valences at the odd carbons are not much larger in the diradical form than in the ground state. There is an interesting discrepancy between the two calculations of the energy necessary to excite the molecule into the triplet state. This suggests that in dealing with these somewhat unusual types of molecule, neither theory is yet completely satisfactory.

The next paper in this group is by Dewar (p. 50). In the last three years Dewar and Walsh have been developing the idea that dative bonds may be formed by donation of an electron from a bond, or even from a whole group of bonds (as e.g. a benzene ring) as well as from an individual atom. Thus some of the organic complexes found experimentally may be the result of interaction between the highly polarisable π-electron shells, or clouds, of the aromatic molecule, and the approaching cation (or anion). The electrons that bind the cation may therefore come from the whole aromatic molecule (e.g. benzene), rather than from any one atom of it. Here are the first explicit calculations to substantiate this argument. As befits such early work, they are tentative, and full of approximations, and, in some cases, doubtful assumptions. But the principle behind them is clear enough. When the cation X^+ comes up to one of these aromatics, the aromatic electrons have an extended freedom since their molecular orbits can now embrace one more nucleus than before. This increases the delocalisation energy, sometimes called resonance energy, though in this case the former title is much the better. It is precisely the additional delocalisation energy that Dewar calculates. This appears to be greater when the approaching group comes up towards the middle of a bond, so that it is under the simultaneous influence of both atoms of the bond, than when it comes up towards one end of the bond and is effectively under influence from only one atom. This is a most interesting paper with relevance to the whole theory of organic reactions; we must hope that some of the approximations and assumptions now inherent in these calculations may be improved, to make the work more quantitatively valid. Some of the difficulties in such calculations are outlined in the paper by Coulson and Dewar on page 54.

THE THEORY OF THE STRUCTURE OF FREE RADICALS.

By C. A. Coulson.*

Received 13th August, 1947.

1. Introduction.

This paper is intended to provide a review of such theoretical calculations as have been made by various authors both of the structure and reactivity of free radicals. It naturally divides itself into two halves; the first half is concerned with alkyl or "saturated" radicals, the second half with conjugated or "unsaturated" ones. The distinction is important because, as we shall see (§ 2), there are characteristic differences between the two types. In the published work concerning the latter radicals there are several different physical and chemical quantities which have been introduced, sometimes under various names for the same quantity, according to the nature of the approximation used in setting up the molecular wave function. Some of these are exactly comparable, others nearly so. We have therefore thought it desirable to gather together (§ 5) the various terminologies and symbols which different authors use (Table III). It is hoped that this table will save confusion, and help to elucidate the original research which forms the substance of almost all the remaining papers in this section of the Discussion.

We conclude the present review with an indication of the chief difficulties in current theory, and a suggestion of those directions in which it seems most likely that future developments may be anticipated.

2. Alkyl Radicals and Conjugated Radicals.

The one really fundamental characteristic of a free radical is that there is one unpaired electron. Whereas all the other electrons are either in localised-pair bonds between two nuclei, or associated in pairs in molecular orbits extending over several nuclei, this one electron is unpaired and available for the formation of some incipient bond with another molecule or radical. Evidently the most significant chemical fact about the radical is the position of this odd electron. It is precisely here that the distinction between saturated and unsaturated free radicals lies. For in an alkyl radical there is only one effective position for the odd electron; in a conjugated one there may be several, leading to a reactivity which is spread over the molecule rather than concentrated almost entirely in one place.

The distinction we have just made is important when we consider molecules such as the phenyl radical C_6H_5 obtained by removal of a hydrogen atom from an aromatic molecule. The unpaired electron is here a σ-type electron which does not possess the characteristic mobile properties of the π-electrons. That is to say, it is effectively localised on the carbon atom from which the hydrogen was originally removed. In its capacity therefore as a free radical, such a molecule must be expected to show the high localised reactivity typical of the alkyl radicals.

However, there are occasions when such a radical does distribute its free valence more widely. We can illustrate this in terms of benzyl $C_6H_5 . CH_2\cdot$, which we may regard as being obtained from toluene by removal of one of the methyl hydrogens. Before removal the appropriate carbon electron was in a σ-state, so that we might at first expect the free valence to be strongly localised. But when the hydrogen atom is

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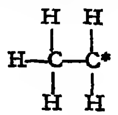
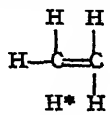
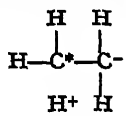
removed, the methyl carbon atom changes its hybridisation from tetrahedral to trigonal, bringing the atoms of the CH_2 group into the plane of the ring. This converts the odd electron from being a σ-type electron to being a π-type electron, and allows it to share the mobile character of the other π-electrons. In this way the free valence is distributed. Also, by virtue of the delocalisation, there is a gain in energy, so that the radical becomes more stable. A situation very similar to this arises in all the free radicals of the triphenylmethyl type. What we have called conjugated radicals are precisely those in which, by some means, the odd electron has a π-type orbit.

We can illustrate the distinction between alkyl radicals with localised free valence, and conjugated ones with distributed valence, by comparing the ethyl radical CH_3—CH_2— and the allyl radical CH_2=CH—CH_2—. In the ethyl radical we may write the structure (I) or any of the three equivalent structures (II). There are also ionic structures such as (III), but these are much less stable than (I) and (II) and need not be considered in a qualitative account. In (I) the free valence (shown by an asterisk *) is on the end carbon atom, in (II) it is on one of the hydrogens. But (I) is much more favoured energetically than

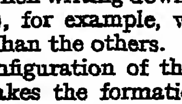

(I)

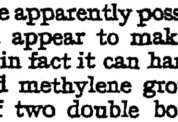

(II)

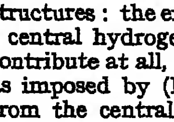

(III)

(II), both because of the high energy of C—H relative to the second bond in C=C, and because the conditions of maximum overlapping of the paired orbits are not very favourable in (II). Consequently (I) predominates, and we may say that the free valence (and hence the reactivity) largely resides in the end carbon atom. There is, however, a small chance of it being found on one of the hydrogens of the methyl group, which we may expect therefore to be a little more reactive than, for example, in ethane. We have here, in fact, the basis of a theory for discussing the relative ease of removal of different H atoms (not protons), but no calculations of this kind appear to have been made.

In the allyl radical, on the other hand, we may write the structures (IV) and (V), both of which are equally important; in addition there are


(IV)


(V)


(VI)

other ionic structures which are less important. In first approximation, therefore, both carbon atoms C_1 and C_3 share the free valence, so that the reactivity is now spread over the molecule. One must be careful, however, when writing down some apparently possible structures: the existence of (VI), for example, would appear to make the central hydrogen more labile than the others. But in fact it can hardly contribute at all, because the configuration of the end methylene groups as imposed by (IV) and (V) makes the formation of two double bonds from the central carbon almost impossible.*

The type of resonance represented by interaction between (I) and (II) seems first to have been mentioned by Wheland.[1] Since the central C—C bond is somewhat strengthened at the expense of some of the C—H

* In order to get two double bonds from a carbon atom, the three nuclei involved should be collinear, as in allene, and the two CH_2 groups would need to be in perpendicular planes, and not, as here, in the same plane.

[1] *J. Chem. Physics*, 1937, **2**, 479.

bonds, the situation bears considerable resemblance to the phenomenon of hyperconjugation discussed by Mulliken, Rieke and Brown.[2] Calculations of the resonance energy for various saturated free radicals (as well as for their positive and negative ions) have been made by Baughan, Evans and Polanyi.[3] Table I, taken from their paper, shows calculated and observed resonance energies, in kcal./mole. These calculations are

TABLE I.

RESONANCE ENERGIES OF ALKYL RADICALS.

Radical.	CH_3.	C_2H_5.	n-C_3H_7.	sec-C_3H_7.	$tert$-C_4H_9.	$(CH_3)_2\!>\!CH.CH_2$
Resonance energy :						
calculated . .	—	7·05	8·6	14·1	21·2	10·2
observed . .	—	7·2	8·1	12·6	16·7	—
Number of structures of type (II) . .	0	3	3	6	9	3

somewhat crude, and too great reliance should not be placed upon the exact values given. There is, as might be expected, a rough correlation between the calculated resonance energy and the number of structures similar to (II). This number is shown in the last line of the table.

3. Alkyl Radicals.

Calculations such as those in Table I are relative; that is to say, *they measure chiefly energy differences rather than absolute values.* If we ask what absolute knowledge is available even for the simplest of radicals, we shall be astonished how little is the answer. We do not even know the energies of removal of successive hydrogens from CH_4 except for the first ($\sim$ 102 kcal.) and the last ($\sim$ 80 kcal.). Even these are obtained by spectroscopic and other experimental methods. The explanation lies in our continuing ignorance of the energies of the various states of the carbon atom, the correct value for whose heat of sublimation is still in dispute. Some detailed analysis by Voge[4] suggests that all four hydrogens should be almost equally easily removed; but these calculations, together with the earlier ones of Van Vleck[5] failed to take adequate account of the change of electronegative character of the carbon atom in its different states of hybridisation; and their wave functions were essentially non-polar. For that reason they are unreliable in detail.

One piece of information, however, does seem reliable. The methyl radical —CH_3 is almost certainly planar[5a, 6] with the HCH angles each equal to 120°. This means that when it is formed by breaking the tetrahedral bond which attaches it to the rest of a molecule, we may anticipate that it will possess considerable vibrational energy. In such a plane radical, the unpaired electron is simply an undisturbed $2p_z$ (or π) electron of a carbon atom. And it will be equally reactive in the two directions perpendicular to the molecular plane.

On the other hand, despite Voge's work,[4] we know effectively nothing about the methylene radical. The original suggestion, that its binding should resemble that in HOH so that the valence angle should be a little greater than 90°, is now believed to be unlikely. Indeed, it is more probably about 140°.[7]

[2] *J. Amer. Chem. Soc.*, 1941, 63, 41.
[3] *Trans. Faraday Soc.*, 1941, 37, 377.
[4] *J. Chem. Physics*, 1936, 4, 581.
[5] *Ibid.*, 1933, 1, 177, 219; 1934, 2, 20.
[6] Bak, *J. Chem. Physics*, 1946, 14, 698.
[7] Herzberg, *Rev. Mod. Physics*, 1942, 14, 195.

Alkyl radicals, of the kind that we are now discussing (methyl, ethyl, etc.) are relatively stable. Their activation energies for decomposition have been calculated by Bawn.[8] They are > 60 kcal. for methyl, and 30-40 kcal. for the others, in fairly good agreement with experiment. The method of calculation may be illustrated by considering the decomposition :

$$CH_3—CH_2—CH_2— \longrightarrow —CH_3 + CH_2{=}CH_2. \quad . \quad . \quad (1)$$

There is, of course, just one energy surface for this reaction, in the language of Eyring, Polanyi and others. But since the details of such a surface are too difficult to compute at all reliably[9] we approximate to the true surface from both sides of the eqn. (1), plotting first the energy surface for the initial distortions of the left-hand side, viz.,

$$CH_3—CH_2—\overset{*}{C}H_2 \longrightarrow \overset{*}{C}H_3 + \overset{*}{C}H_2—\overset{*}{C}H_2,$$

and, second, the final distortions as we reach the right-hand side; i.e. we plot the interaction between the two distinct groups $—CH_3$ and $CH_2{=}CH_2$. By superposing the two energy diagrams thus calculated we can estimate the height of the potential barrier involved in (1). Unfortunately so many factors receive inadequate attention in all treatments of this sort (e.g. resonance in the activated-complex transition state) that the final values for the activation energy have only the status of a "semi-empirical" calculation.[9] But they do give insight into the processes involved.

4. Conjugated Free Radicals.

The general situation as regards conjugated free radicals is much happier than as regards alkyl radicals. Our theoretical knowledge of these radicals falls into three clearly marked stages :

(a) energy, 1932-1939 ;
(b) shape, or structure, 1939-1945 ;
(c) reactivity, 1945- .

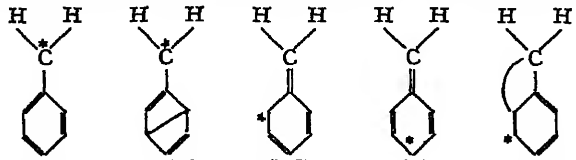
It will be best to discuss each of these stages separately, and to illustrate them, where possible, in terms of the same particular example. We shall take this to be the phenylmethyl, or benzyl, radical $C_6H_5 . CH_2$. As in all problems concerned with conjugated systems, there are two distinct types of approximation. Fortunately in almost every case the two theories give equivalent results. But they arrive at these results in a slightly different way, using distinct notations and terminology. We shall therefore illustrate them both. This can best be done by taking the stages (a), (b) and (c) separately, and in that order.

(a) Energy Calculation.—Early work on free radicals was entirely concerned with their stability; that is, with calculating their energy. Thus hexa-aryl ethanes dissociate into two radicals of Gomberg type if the total energy of these radicals is sufficiently low relative to the original molecule. The extra stability is here attributed to the possibility of planar radicals, in which resonance among the π electrons may take place. Such planarity is not possible, for example, in C_2Ph_6, but it is nearly possible in CPh_3, and leads to a lowering of the total energy. This lowering is, in fact, simply the resonance energy of the two radicals, together with additional terms arising from the changed valence conditions—tetrahedral to trigonal hybridisation[10]—around the carbon atom, and the changed steric effects between non-bonded hydrogen atoms in the two

[8] *Trans. Faraday Soc.*, 1938, 34, 598.
[9] Hirschfelder, *J. Chem. Physics*, 1941, 9, 645.
[10] Coulson, *Proc. Roy. Soc. Edin.*, *A*, 1941, 61, 115.

systems. It is important to note that although this latter energy may amount to as much as 30 kcal.[11] it cannot possibly provide by itself the energy necessary to break the central C—C link in a molecule like C_2Ph_6.

The resonance energy is interpreted differently according as we use the valence-bond (v.b.) method of resonance among canonical structures, introduced by Pauling,[12] or the molecular orbital (m.o.) method introduced in this connection by Hückel.[13] Let us take the case of benzyl to illustrate, assuming as usual that the molecule is completely planar.



(VII) (VIII) (IX) (X) (XI)

The v.b. method regards the complete wave function for the molecule as a linear combination of wave functions representing the various structures such as (VII)-(XI), each of which corresponds to a certain method of pairing the π electrons. In each structure there is one unpaired electron (shown with an asterisk *) which, for purposes of calculation, is regarded as paired with a " phantom " electron at infinity. In (VII) and (VIII) which by analogy with benzene we may call Kekulé and Dewar structures, the free electron is at the methyl carbon: in (IX) and (X) the free electron is at an atom of the benzene ring. Resonance among structures (VII) and (VIII)—there are two of type (VII) and three of type (VIII)—gives the resonance energy of benzene. We can now see why there is additional stability in the radical, for the structures (IX) and (X) have no counterpart in benzene. There are other, more excited, structures, such as (XI), but as Mme. Pullman shows in a later paper in this Discussion [14] for the polyene chain radicals, these excited structures are not as important as in the parent hydrocarbons; we may therefore neglect them. If we call the various structures ϕ_1, ϕ_2, . . . then the complete wave function ψ is written in the form:

$$\psi = c_1\phi_1 + c_2\phi_2 + \dots \qquad (2)$$

where the c_r are constants found by a perfectly definite mathematical technique.[12] The corresponding energy is also found, results being expressed in terms of the so-called exchange integral α (or J). This is a constant which corresponds to the integral introduced by Heitler and London in their first treatment of the H_2 molecule. Its value cannot here be found by *a priori* calculation, but is estimated from observed heats of combustion and hydrogenation. For C—C bonds α is about -37 kcal. In benzyl the resonance energy is approximately $-0{\cdot}51\alpha$ greater than in benzene. This represents the additional stability on account of the inclusion of structures such as (IX) and (X). Pauling and Wheland [15] show that in fact individual structures of type (VII) are about the same importance as individual structures of types (IX) and (X).

In the m.o. method each of the 7 π-electrons moves over the complete carbon skeleton; there are four molecular orbits,[16] three of which are bonding and are occupied by two electrons each. The fourth molecular orbital is neither bonding nor anti-bonding, and is half-filled with the remaining odd electron. The total energy is found by perfectly definite

[11] Bent and Cuthbertson, *J. Amer. Chem. Soc.*, 1936, **58**, 170.
[12] *J. Chem. Physics*, 1933, **1**, 280.
[13] *Z. Physik*, 1931, **70**, 204; 1932, **76**, 628.
[14] Pullman, this Discussion, p. 26.
[15] *J. Chem. Physics*, 1933, **1**, 362 (Table IV), as corrected by Pullman in her paper on p. 30.
[16] Lennard-Jones and Coulson, *Trans. Faraday Soc.*, 1939, **35**, 811.

rules [13, 17] and the resonance energy is given in terms of a resonance integral β (or γ). β is not the same as α, and has a numerical value about -20 kcal. As with α this value is obtained by comparison with experimental heats of formation and hydrogenation, and not by direct calculation. Values of the additional resonance energy, over and above that of the parent hydrocarbons, in a few simple radicals are shown in Table II, taken from Wheland.[18]

In this way we can draw up a list showing the order of increasing dissociation of the various aryl ethanes. With one or two exceptions, this is the same as the order found experimentally.

TABLE II.

FREE RADICAL RESONANCE ENERGIES.

Radical.	Valence-bond Method.	Molecular-orbital Method.
phenyl methyl .	$-0{\cdot}51\alpha$	$-0{\cdot}72\beta$
diphenyl methyl .	$-0{\cdot}84\alpha$	$-1{\cdot}30\beta$
triphenyl methyl .	$-1{\cdot}11\alpha$	$-1{\cdot}80\beta$
α-naphthyl methyl .	$-0{\cdot}75\alpha$	$-0{\cdot}81\beta$
β-naphthyl methyl .	$-0{\cdot}63\alpha$	$-0{\cdot}75\beta$

Certain refined calculations are possible. Thus Coulson [19] has discussed the effects of allowing different values of β for the various links, using a principle established by Lennard-Jones.[20] He was able to plot the energy of the allyl radical in terms of the lengths x_1 and x_2 of the two carbon-carbon bonds. Orr (quoted by Bolland and Gee [21]) has recalculated some of Coulson's radicals using revised fundamental bond energies. He finds the following resonance energies for a polyene chain of n carbon atoms of formula C_nH_{n+2}.

n	3 (allyl)	4 (butadiene)	5 (pentadienyl)
resonance energy (kcal.)	18·7	6·9	30·4

The additional stability of the free radicals (n odd) is very marked. Other refinements which, however, do not alter the general results, have been made by Wheland [22] using the m.o. method, and by Penney and Kynch [23] using the v.b. method.

(*b*) **Structure and Shape.**—In order that the molecules may all be planar, the carbon atoms are all in a trigonal state, and the angles are practically all about 120°. But the bond lengths are not necessarily all equal. Except for the smaller molecules, for which Coulson [19] has calculated by direct m.o. methods the lengths of all the links, it has been found necessary to determine bond lengths by means of bond order. The bond order is calculated, and the length is read off from a curve connecting order and length.

In m.o. calculations there is a quite simple definition of bond order [24] Each mobile electron contributes a partial bond order to each C—C bond, and the total mobile order for any bond is simply the sum of these partial orders. In v.b. calculations the bond order is most easily obtained by a method due to Pauling, Brockway and Beach,[25] though for simple molecules a refinement is possible.[26] The method of Pauling, Brockway and Beach uses formula (2) for the complete wave function, and interprets it to mean that structure number 1 (ϕ_1) has a weight $c_1^2/(c_1^2 + c_2^2 + \ldots)$, etc. The mobile bond order of a bond connecting two given atoms is

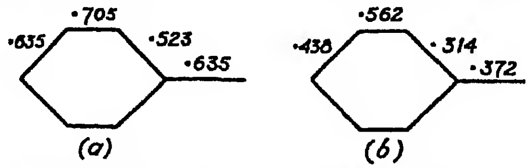
[17] Hückel, *Z. Physik*, 1933, **83**, 632 ; *Trans. Faraday Soc.*, 1934, **30**, 40.
[18] *Ann. N. Y. Acad. Sci.*, 1940, **40**, 77.
[19] *Proc. Roy. Soc. A*, 1938, **164**, 383.
[20] *Ibid.*, 1937, **158**, 280.
[21] *Trans. Faraday Soc.*, 1946, **42**, 244.
[22] *J. Amer. Chem. Soc.*, 1941, **63**, 2025.
[23] *Proc. Roy. Soc. A*, 1938, **164**, 409.
[24] Coulson, *ibid*., 1939, **169**, 413.
[25] *J. Amer. Chem. Soc.*, 1935, **57**, 2705.
[26] *Proc. Roy. Soc. A*, 1937, **158**, 306.

then the total weight of all structures in which this bond appears double. Provided that one takes sufficient structures into account, this method gives quite good results.

The quantity we have called bond order is sometimes called double-bond character and expressed as a percentage; sometimes also *indice de liaison*. At one time, following a suggestion of Svartholm,[27] twice the bond order was called the *charge de liaison*; but this was not a happy notation, and is now abandoned. The papers by Pullman [14] and Daudel [28] in this Discussion, show values of the *indice de liaison* for molecules C_nH_{n+2} and for various derivatives of triphenylmethyl. Moffitt and Coulson [29] have refined these calculations somewhat, and Coulson and Longuet-Higgins [30] have shown that the rth carbon-carbon bond in a free radical C_nH_{n+2} where n is odd, has mobile order (m.o.):

$$p_r = \frac{1}{n+1}\left\{\cot\frac{\pi}{2n+2} + (-1)^{r-1}\cot\frac{(2r+1)\pi}{2n+2}\right\}.$$

The mobile bond orders calculated for benzyl by Coulson (unpublished m.o.) and Mde. Pullman [14] (v.b.) are shown in Fig. 1. These two diagrams give qualitatively similar descriptions of bond order and length. It is important to realise that as the two definitions of bond order are not equivalent, there are two curves relating order and length, one for m.o. and the other for v.b. use. It appears that the m.o. orders are always numerically greater than or equal to the v.b. ones. This does not



(*a*) molecular-orbital (*b*) valence-bond

FIG. 1.—Mobile Bond Orders in Benzyl.

N.B.—The two definitions of bond order are not the same, so only relative values in (*a*) and (*b*) are significant.

matter provided that we know in which system the calculations are made. The actual bond lengths predicted for benzyl do not differ much for the two methods, and no sufficiently detailed experiments are available with which to check either. But, working from left to right in Fig. 1, the average values [31] are 1·39, 1·38, 1·41, 1·38 A.

(*c*) **Reactivity.**—The most important recent development in the theory of the reactivity of organic molecules generally has been an attempt to provide numerical values by which the absolute reactivities of different positions may be estimated. Free radicals are included in this type of analysis. In this case the reactive centres are evidently those on which the unpaired electron spends most of its time. In m.o. language, if we regard the unpaired electron as describing a molecular orbit which covers all the nuclei, it may be shown [29] that this electron is concentrated solely on alternate carbon atoms, beginning at the end ones, and is evenly divided among them, in chain molecules C_nH_{n+2}. Thus the odd electron spends $2/(n+1)$ of its time on each of the $(n+1)/2$ carbon atoms 1, 3, 5 . . . and none of its time elsewhere. This explains why longer radicals of this kind are less reactive than shorter ones: for at any one atom the fractional unpaired charge is decreased if the chain length is increased. A very similar result is predicted (see later) by Mde. Pullman [14]

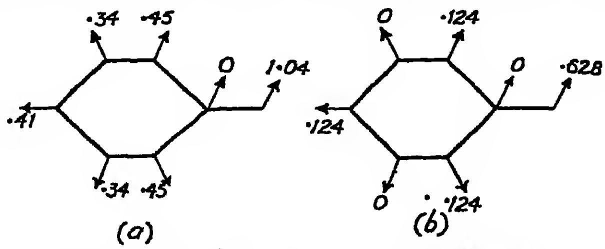
[27] *Arkiv. Kemi. Min. Geol.*, 1942, 15, No. 13.
[28] *Trans. Faraday Soc.*, this Discussion.
[29] *Ibid.*, 1948, 44, 81.
[30] *Proc. Roy. Soc. A* (in press).

using v.b. theory. This alternate distribution of the odd electron holds in all common hydrocarbon radicals, including benzyl, though the uniformity of distribution is confined to the chain radicals. In benzyl the odd electron is distributed among the end carbon and the two *ortho* and the *para* positions of the ring in the ratio 4 : 1 : 1 : 1. In the presence of 5-membered rings [31] and in hetero-radicals, the alternate distribution will generally not hold, but no calculations have yet been reported. In some ways this interpretation of reactivity is parallel to one given by Hückel [13b] for non-radical hydrocarbons such as naphthalene, anthracene, etc.

But if we suppose that the other π electrons as well as the unpaired one contribute to the free valence, we may proceed as follows.[32] Consider (Fig. 1*a*) one of the *meta* carbons in benzyl. This atom is forming bonds of total order 1·635, 1·705 and 1·0; the first two are C—C bonds and the third is C—H. We may define its total bond number N as

$$N = 1{\cdot}635 + 1{\cdot}705 + 1{\cdot}0 = 4{\cdot}340.$$

N measures the total degree of bonding of this atom. Now the maximum value of N found so far for carbon in any molecule is 4·680. So we could



(*a*) molecular-orbital (*b*) valence-bond

FIG. 2.—Free Valence in Benzyl.

N.B.—The two definitions of free valence are not the same, so only relative values in (*a*) and (*b*) are significant.

introduce the free valence F of this atom [33] as the "residual affinity" (in the language of Werner), and write

$$\begin{aligned} F &= N_{max} - N \\ &= 4{\cdot}680 - 4{\cdot}340 = 0{\cdot}34. \end{aligned}$$

A convenient notation for the free valence is an arrow, as shown in Fig. 2*a*, leading away from the atom, with the magnitude of F attached. This would distinguish the free valence from the net charge at the atom, which could be represented by a number attached without an arrow to the atom concerned. In the case of our hydrocarbon radicals the net charge is either exactly, or practically, zero. In benzyl the most reactive centres are just those one would have expected. It seems likely that the best picture of the reactivity of benzyl lies somewhere between the two accounts just given. That is to say, it is due not entirely to the one unpaired electron, but partly also to the other π electrons, since no one electron in a molecule can ever be treated entirely independently of the others.

The idea of free valence may be extended to v.b. theory, and calculations for various hydrocarbons have been made by Daudel, Pullman and collaborators [34] under the former title *charge du sommet*, now altered to the more accurate description *indice de valence libre*. In the case of hydro-

[31] Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193.
[32] Coulson, *Trans. Faraday Soc.*, 1946, **42**, 265.
[33] Coulson, *ibid.* (in course of publication).
[34] P. and R. Daudel, Jacques and Jean, *Rev. Sci.*, 1946, **84**, 489; A. Pullman, *Thesis* (Paris, 1946).

carbons P. and R. Daudel and Coulson [35] have shown that the two treatments are very similar in their conclusions. Mme. Pullman [14] gives similar results for benzyl (shown in Fig. 2b) and the odd-membered chains, in this Discussion. The free valence, or *indice de valence libre*, is now defined in a way entirely analogous to that used for bond orders. It is the sum of the weights of all structures in which the chosen atom is not joined by a double bond to one or other of its nearest neighbours.

In this way a beginning has been made in a quantitative study of the homolytic reactivity of hydrocarbon free radicals. Some work by Coulson and Longuet-Higgins [30] has shown how heterolytic reactivity may be similarly studied in m.o. approximation, but applications to free radicals have not yet been made.

5. Synthesis of Terminology and Symbols.

Table III shows the significance of the various symbols and terms that have been proposed from time to time. The table itself is self-explanatory.

TABLE III.

TERMINOLOGY AND SYMBOLS USED BY DIFFERENT WRITERS

	Valence-bond.	Molecular Orbital.
Resonance energy arises from	Resonance among canonical structures	Delocalising of electrons into orbits over the whole molecule
Resonance energy measured in units of . . .	Exchange integral α (sometimes called J)	Resonance integral β (sometimes called γ)
Bond lengths defined by .	Mobile bond order $\equiv$ double-bond character, also *indice de liaison*, formerly one-half of *charge de liaison*	Mobile bond order which is the sum of partial bond orders of all π-electrons
Homolytic reactivity determined by . . .	Free valence, i.e. *indice de valence libre*, formerly *charge du sommet*	Free valence F, where $F = N_{max} - N$, and N = total bond number (For C atoms $N_{max} = 4{\cdot}680$).
Heterolytic reactivity determined by . . .	Total net charge on the atom, sometimes called *charge totale*	(a) Total mobile charge (b) Self-polarisability of the atom.[30]

6. Future Developments.

It may perhaps be permitted to close with an indication of some of the lacunæ in present theory, and of the directions in which we may anticipate progress in the near future.

First of all, in all resonance calculations, whether with alkyl or conjugated radicals, we must include ionic structures: for without these no valid discussion of the energy of heteromolecules is possible, and no estimate can be made of the polarisability of one molecule or radical due to the approach of another; that is, no satisfactory quantitative measure of heterolytic reactivity is possible, and even that of homolytic reactivity is somewhat uncertain.

Next, in all m.o. calculations, adequate allowance must be made for electron-repulsion terms, without which we necessarily exaggerate all charge-transfer and polarisability effects.

In both theories a deeper understanding is desirable of the relation

[35] *Rev. Sci.*, 1947, 85, 29.

between free valence and reactivity. This will almost certainly involve a deeper discussion of the transition complex.[36] We also require to know why, although both the v.b. and m.o. theories show such excellent relative agreement, the ratio of the two fundamental parameters α and β (see Table III) required to give absolute agreement is only about 1·3 for free radicals, although it is nearly 2·0 for other conjugated systems.[37]

Questions relating to the dissociation into pairs of radicals of such molecules as the hexa-aryl ethanes cannot adequately be discussed in an absolute manner until we have more detailed information regarding the steric forces between non-bonded atoms, particularly hydrogen.

In both v.b. and m.o. calculations adequate account is still not taken of the change in atomic radius and electronegativity of a carbon atom according to the nature of its hybridisation.[38] Partly also for this reason, we still have no completely adequate account of hyperconjugation, without which the theory of alkyl radicals developed in § 2 is largely empirical. Such an account, if expressed in v.b. language, must discuss the geometrical conditions under which the valence requirements of structures such as (I) and (II) can be simultaneously satisfied. This again requires a deeper understanding of what is meant by a localised, or non-localised bond; and, in the case of carbon, more knowledge of the energy of its various valence states.

Although the above list sounds formidable, there does not seem to the writer any fundamental reason why progress should not be made: and we may expect the resolution of at least some of these difficulties, even with our present knowledge, in a not-too-distant future.

Résumé.

On présente ici une revue des calculs théoriques se rapportant à la structure et à la réactivité des radicaux libres alcoyles (ou saturés) et aromatiques (ou non saturés). On compare les terminologies et symboles divers employés dans les travaux sur les radicaux aromatiques. On indique les principales difficultés rencontrées dans les théories courantes et l'on suggère de futurs développements.

Zusammenfassung.

Der Artikel gibt einen Überblick über Berechnungen der Struktur und Reaktivität von sowohl Alkylradikalen (gesättigt) als auch aromatischen (oder ungesättigten) freien Radikalen. Die verschiedenen Terminologien und Symbole, die in Arbeiten über Arylradikale verwendet werden, werden verglichen. Die Hauptschwierigkeiten bei den gegenwärtigen Theorien werden angedeutet und Vorschläge für weitere Entwicklungen gemacht.

Physical Chemistry Laboratory,
Oxford.

[36] Wheland, *J. Amer. Chem. Soc.*, 1942, 64, 900.
[37] Wheland, *J. Chem. Physics*, 1934, 2, 474.
[38] Coulson, *V. Henri Memorial Vol.* (Liège) (in press).

THE PROPERTIES OF BONDS INVOLVING CARBON.

By A. D. Walsh.

Received 18th August, 1947.

It is well known that the *s, p, d*, . . . nomenclature for describing the forms of electronic orbitals in free atoms is not always suitable for the description of valency orbitals employed in molecule formation. For

example, in most of its compounds, carbon uses valencies which may be described as hybrids of its 2s and 2p atomic wave functions. As a result of this hybridisation, a carbon atom in a molecule has an important flexibility. The properties of a carbon valency change as the degree of hybridisation changes. Thus its electronegativity changes and, with it, changes the strength of the bond formed by the valency. In conformity with the requirement of minimisation of free energy, therefore, a carbon atom adjusts itself to the particular environment in which it lies. The properties of any carbon valency (for example, the length and direction of the bond it may form) are always specific to a particular valency in a particular atom in a particular molecule. Additivity rules (such as the idea of constant CH bond energies) are only approximate. In some cases the differences are too small to be detected, but in others they are now well established. It is the purpose of this paper to show how these differences can be correlated with change in the degree of hybridisation involved. This approach has already been used outstandingly by Coulson.[1] It translates into other language the approach in terms of electronegativities and polarities previously attempted by the author,[2, 3, 4, 5] but in doing so reveals further important correlations and explanations. Particular application is made here to the CH, CH_2 and CH_3 radicals.

Fundamental Principle.

The more s *Character in a Carbon Valency, the more Electro-negative is the Carbon Atom in that Valency.*

This principle is strongly supported by (*a*) the body of facts (see below) that follow from it in close accord with experiment (*b*) theoretical work of Coulson[1] which shows the average distance of an electron from the nucleus to be greater in a 2*p* than in a 2*s* orbital: which is to say that the "pull" or electronegativity of a carbon atom is greater when it is exerting a 2*s* than a 2*p* valency.

Application to Polarity of Carbon Bonds.—The type of hybridisation involved in the carbon valencies towards hydrogen in methane, ethylene and acetylene is well known and is listed in Table I. The bond in the CH radical probably uses a pure *p* carbon valency: evidence for this is either to be found in a theoretical paper by Coulson[1] or in the agreement of the hypothesis with our discussion below of CH bond strengths. The molecules in Table I are listed in such a way that the proportion of *s* character in the carbon valency towards hydrogen increases as we pass downwards. Application of our fundamental principle therefore means that the carbon electronegativity towards hydrogen also increases as we pass downwards. In methane the CH bond dipole is known to be small and to have the direction $C^{\delta+}H^{\delta-}$.[6, 7, 8] We may hence expect that on passing from methane to ethylene a reversal of polarity direction occurs, so that the CH bonds of ethylene have a small bond dipole of sign $C^{\delta-}$–$H^{\delta+}$. On passing from ethylene to acetylene, instead of reversal of sign, an intensification of the $C^{\delta-}$–$H^{\delta+}$ polarity takes place so that acetylenic CH

TABLE I.

Molecule.	C Valency towards H.
CH radical	*p*
CH_4	sp^3
C_2H_4	sp^2
C_2H_2	*sp*

[1] Coulson, *V. Henri Memorial Vol.* (Liège) (in press).
[2] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 56.
[3] Walsh, *ibid.*, 1947, **43**, 60.
[4] Walsh, *ibid.*, 1947, **43**, 158.
[5] Walsh, *J. Chem. Soc.* (in press).
[6] Coulson, *Trans. Faraday Soc.*, 1942, **38**, 433.
[7] Gent, *Nature*, 1946, **158**, 27.

bonds have a comparatively high bond dipole of sign $C^{\delta-}H^{\delta+}$. Thus we explain, very simply, the acid nature of acetylene and the high electron-attracting nature of a C≡C— group as evidenced by the much greater dissociation constant of propiolic than of acrylic acid and by studies of the velocity of reactions involving electron accession to the reaction centre.[8] We also explain the lowered polarity of the carbonyl group in ketene relative to formaldehyde,[9] for the central carbon atom of ketene is an acetylenic one, forming two σ bonds (in line) and two π bonds.

Passing *upwards* in Table I from methane to the CH radical, an intensification of the $C^{\delta+}H^{\delta-}$ polarity takes place, so that the CH radical is expected to have a high bond dipole of sign $C^{\delta+}H^{\delta-}$.

Conversely, one may say that if an X_3C—Cl bond has a markedly lower dipole moment than the bond in the corresponding alkyl chloride, the carbon valency in X_3C—Cl towards chlorine has appreciably more *s* character than has sp^3. This argument (comparing the dipole moments of cyclopropyl and *iso*propyl chlorides) has been employed [10] to show that the carbon valencies towards hydrogen in cyclopropane are nearer the trigonal (sp^2) than tetrahedral (sp^3) type.

Application to Strengths of Carbon Bonds.—One of the most important factors determining the strengths of bonds lies in the electronegativity of the bonded groups. Normally the bond strength increases with increase in the product of the electronegativities of the bonded groups. This fact has been stressed by Gordy,[11] though there are exceptions which can be understood.[5] It follows that we expect the CH bond strength to increase as we pass downwards in Table I. That this is so is shown by Table II: the direction of change in the lengths (r), stretching-force constants (k) and energies (E) of the CH bonds are all in agreement and all show that the bond strengthens with increase in the *s* character of the hybrid carbon valency employed. (The further factor determining bond strength—namely that the strength is reduced with increase of polarity [2, 3, 4, 5]—means that the difference in strength between $CH_{rad.}$ and CH_{CH_4} is somewhat magnified while that between $CH_{C_2H_4}$ and $CH_{C_2H_2}$ is somewhat reduced.)

TABLE II.

Molecule.	r(CH) Å.	k(CH) dynes/cm.	E(CH) kcal./mole.
CH radical	1·120	$4·09 \times 10^5$	80
CH_4	1·094	4·79	~ 104[12]
C_2H_4	1·087	5·1	~ 106[13]
C_2H_2	1·059	5·85	~ 121[14]

Further Applications.

If in the compound $XCR_1R_2R_3$ we change X for a group of higher electronegativity, then, clearly, the effective electronegativity of the carbon atom towards the groups $R_1R_2R_3$ must be increased. In other words the valencies of the carbon atom towards $R_1R_2R_3$ must have increased *s* character. This in turn means that the carbon valency towards X has increased *p* character. An alternation becomes apparent. Our fundamental principle therefore carries with it the following corollary.

[8] Braude and Jones, *J. Chem. Soc.*, 1946, 128.
[9] Walsh, *J. Amer. Chem. Soc.*, 1946, 68, 2408.
[10] Walsh, *Nature*, 1947, 159, 712.
[11] Gordy, *J. Chem. Physics*, 1946, 14, 305.
[12] Long and Norrish, *Proc. Roy. Soc. A*, 1946, 187, 337.
[13] Value assigned as explained below.
[14] Cherton, *Bull. Soc. Sci. Liége*, 1942, 11, 203.

If a Group X attached to Carbon is replaced by a more Electro-negative Group Y, then the Carbon Valency towards Y has more p *Character than it had towards X.*

This subsidiary principle is a translation into quantum-mechanical language of the well-known charge transfer or inductive effect.* The translation is well worth making for it indicates new properties (in terms of bond angles, stretching and bending-force constants, bond lengths and energies) of the inductive effect. It gives a very simple explanation of many facts that have come to light in recent years and which hitherto have been puzzling. To take two examples.

(1) If a hydrogen atom of methane is replaced by chlorine, then the carbon valencies towards the three remaining hydrogen atoms have increased *s* character. The CH bonds should therefore be slightly stronger in CH_3Cl than in CH_4: we have already given thermochemical evidence that this is the case.[3] Considering in CH_3Cl the three carbon valencies towards hydrogen, they should show an approach from sp^3 character towards the hybrid valencies of ethylenic carbon atoms; that is, they should show some approach towards a planar, 120° inter-valency angle, arrangement. The finding of Bak[16] that the methyl group in CH_3Cl is flatter than in methane is thus simply explained. Again, since an *s* orbital is spherically symmetrical while a *p* orbital has strong directional properties, the CH bonds of methyl chloride should show less resistance to deformation than those of methane. That is, the CH bending-force constant should be less in methyl chloride than in methane,[17] though the converse should be true of the CH *stretching*-force constant. Sheppard and Sutherland[18] have shown that the force constant for the out-of-plane bending of CH in RCH=CHR gets less as the electronegativity of R increases. This is in full accord with the theory developed here.

(2) Propane can be derived from CH_4 by replacing two H atoms by the less electronegative CH_3 groups. Each central C valency to H has therefore more *p* character (so explaining the weakness of 2° CH bonds[3, 19]), while the CC valencies have more *s* character and should be more linear. Electron diffraction shows that the CCC angle is greater than tetrahedral in propane (114°[20]).

Application to the CH_3 Radical.

When a carbon atom is attached to only three atoms, as in the methyl radical, the strongest bonds will be formed when the carbon valencies are of the planar, 120° type (cf.[21]). There is some experimental evidence in accord with this, utilising the theory of optical activity.[22] In consequence the CH bonds of free methyl should be slightly stronger than those of methane (cf.[23]). It is a merit of the Long and Norrish[12] use of ~ 190 kcal./mole for the heat of sublimation of carbon in calculating heats of atomisation (whatever the precise interpretation to be put upon

* The principle is readily extended to valencies of atoms other than carbon. Thus P in PF_5 uses hybrid sp^3d valencies. If therefore we change an F for Cl, we expect more *s* in the P valency to Cl and more *p* or *d* character in the P valencies to F. Hence *r*(PF), should be shorter in PF_3 than in, say, PF_3Cl_2. Brockway and Beach[15] report *r*(PF) = 1·59 ± 0·03 A. in PF_3Cl_2 and 1·57 ± 0·02 A. in PF_5.

[15] Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836.

[16] Bak, *J. Chem. Physics*, 1946, **14**, 698.

[17] For evidence that this is so compare Herzberg, *Infra Red and Raman Spectra* (Van Nostrand, 1945), and Duchesne, *Nature*, 1947, **62**, 159.

[18] Sheppard and Sutherland (in course of publication).

[19] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 269.

[20] Bauer, *J. Chem. Physics*, 1936, **4**, 406.

[21] Voge, *ibid.*, 581.

[22] See Waters, *The Chemistry of Free Radicals* (Oxford, 1946), p. 175.

[23] Van Vleck, *J. Chem. Physics*, 1934, **2**, 20.

this figure) that it is chosen to be in accord with this expectation for the CH bond strength in free methyl. For the energy required to dissociate a hydrogen atom from methane is about 102 kcal./mole,[13] so that the bond energies in free methyl and methane become $\sim$ 105 and $\sim$ 104 kcal./mole respectively.

The polarity of the bonds in free methyl is expected to be $C^{\delta-}H^{\delta+}$. We may therefore expect replacement of an H in free methyl by a trigonal carbon atom to evoke a little more *s* character in the valencies of the carbon atom towards hydrogen. That is, the carbon atoms of ethylene cannot, because of the lack of symmetry, be examples of "perfect" trigonal atoms. The CC σ bond will have very slightly more *p-p* character than sp^2-sp^2, the angle HCH should be very slightly greater than 120° and the angle HCC very slightly less than 120°. Also the CH bonds of ethylene should be slightly stronger than in free methyl.* A suitable energy value to assign to them would be 106 kcal. (as has been done in Table II) because this value then accords with the Long and Norrish implied value of the free methyl bond energy and also with plots of bond energy against other bond quantities such as bond strength.

The planarity of the free methyl radical may also be supported by the following argument. If X replaces H in CH_4 and X is supposed to increase in electronegativity, then the carbon valency towards X (beginning as sp^3) will increase in *p* character, until, when X has infinite electronegativity (and has therefore completely removed the two electrons in the CX bond), the carbon valency towards X has reached its limit of pure *p* character. The remaining carbon valencies must then be sp^2 in type. That is, the free methyl positive ion must be planar. Adding an electron (to form the free methyl radical) will not disturb this configuration, the electron simply passing into the vacant *p* orbital. Hybridisation of this orbital will only occur when a *bond* is formed from the CH_3, for hybridisation is a phenomenon which occurs by virtue of the energy lowering due to increased atomic orbital overlap which it makes possible. With a free valency considerations of atomic orbital overlap do not enter: that is why valency hybridisation is a molecular phenomenon and is irrelevant for free atoms. In CH_3Cl we have a stage intermediate to CH_4 and to the case where X has infinite electronegativity; so that the work of Bak [18] confirms our argument by showing that the CH_3 group is then intermediate to the tetrahedral and planar configurations.

Application to the CH_2 Radical.

If CH_2 is considered as formed from divalent carbon, two pure *p* valencies of the carbon might be expected to be used, there being no unpaired electrons, the angle HCH being 90° and E(CH) being $\sim$ 80 kcal./mole as in the CH radical. If so our discussion shows that the CH bonds would be heavily polar with the sign $C^{\delta+}H^{\delta-}$. Repulsion of the negatively-charged hydrogen atoms would then be expected to increase considerably $H\widehat{C}H$. Putting this in other language, the proportion of *s* character in the C valencies would increase from zero. Simultaneously, the CH bond strength would increase both because of the reduction of polarity and because of the increase in electronegativity product for each bond. Increase of stability because of these factors and because of reduction of H—H repulsion mean that we can expect that C in CH_2 employs valencies that are not pure *p* but contain rather considerable *s* character.

Some sort of energy hurdle for this hybridisation would need to be postulated in order to explain why the C valency in the CH radical apparently remains pure *p* in spite of the possibility of reducing bond

* Inclusion of the effect of the π bond may upset these conclusions, for it tends to "tighten" the σ bond, i.e. to increase its *s-s* character. All we can perhaps fairly conclude is that $E(CH)_{CH_3}$ is close to $E(CH)_{C_2H_4}$.

polarity and increasing bond electronegativity product by hybridisation: in CH_2 the gain of energy by these factors applied to *two* bonds and by reduction of H—H repulsion may then be supposed to be greater than the hurdle height, whereas in the CH radical with only *one* bond to strengthen and no repulsion to remove, the possible gain may well be less than the energy hurdle. The agreement of our expectations (see below), based upon the occurrence of valency hybridisation in CH_2, with what experimental facts are available *necessitates* the supposition of this energy hurdle opposing hybridisation. If we suppose that the hurdle is the energy required to remove the pairing of two electrons in a lone-pair orbital on the C atom of CH or CH_2 (appreciable hybridisation only occurring in conjunction with this *) i.e. that it is related to the energy difference of the ^3P and ^5S states of atomic carbon, then we shall expect the ground state of CH_2 to contain two unpaired electrons. This expectation does not appear to be impossible (see below). Long and Norrish [12] stress the existence, as C is converted into CH_4, of an energy hurdle related to the ^3P—^5S *transition in atomic carbon but (a) they suppose it lies in that* part of the course which is between CH_2 and CH_3 (whereas we tentatively suppose it to lie between CH and CH_2), and (*b*) they not only relate, but also *equate*, it to the magnitude of the ^3P—^5S transition energy (which seems uncertain since the latter refers to a happening in a free atom and the hurdle refers to an event in an atom bound in a CH or CH_2 molecule).

Two factors are concerned in the strengths of the bonds in CH_2: (*a*) the electronegativity difference and (*b*) the electronegativity product in the bonds. The first causes the C valencies to avoid the extreme possibilities of pure p (high $C^{\delta+}H^{\delta-}$ polarity) and sp (high $C^{\delta-}H^{\delta+}$ polarity). The second causes the valencies to be as near to sp as possible. The compromise structure is therefore expected to have an angle nearer to 180° than to 90°.

Herzberg [24] has suggested, with some justification, that the group of bands observed near 4050 A. in the spectra of comets may be ascribed to CH_2. These bands have been reproduced in the laboratory by Herzberg [25] using an electrodeless discharge in a stream of CH_4 and by Hermann [26] using a discharge between C electrodes in an atmosphere of H_2 greatly diluted by inert gas. This work makes it certain that the bands are due to a hydrocarbon and renders Herzberg's attribution of them to CH_2 very plausible. Accepting this identification, the structure of the bands yields a moment of inertia for CH_2 which, in turn (whatever plausible value one takes for r(CH)) leads to an HCH angle of *ca.* 145°. The magnitude of this is consistent with our discussion of the motivating force for the widening. A graph of $r(\mathrm{CH})$—$\widehat{\mathrm{HCH}}$ for CH_4, C_2H_4 and C_2H_2 yields the value $r(\mathrm{CH})_{CH_2} \sim 1{\cdot}074$ A. for $\widehat{\mathrm{HCH}}_{CH_2} = 145°$; whilst a graph of r(CH)—E(CH) for the same molecules yields a value for $E(\mathrm{CH})_{CH_2}$ of ~ 115 kcal./mole.

Now if CH_2 had a linear structure (employing two sp C valencies at 180°), it would have two pure p orbitals of equal energy. Because of this degeneracy, by the principle of maximum multiplicity (which results, for

* In carbon monoxide, the carbon valency in the σ bond appears to show sp hybridisation.[27] The "driving force" for this is the same as in CH_2, namely, the increase of bond strength by reduction of polarity and increase of bond electronegativity product; but it occurs without splitting the lone pair on the carbon atom because the only orbitals available for these "atomic" electrons are one of sp and one of pure p character, which are far from degenerate. The low dipole moment of CO is a very natural result of the flexibility of a carbon atom resulting from hydridisation. Similarly, we expect the bonds in CH_2 to have low polarity.

[24] Herzberg, *Rev. Mod. Physics*, 1942, 14, 195.
[25] Herzberg, *Astrophys. J.*, 1942, 96, 314.
[26] Hermann, *Compt. rend.*, 1946, 223, 280.
[27] Long and Walsh, *Trans. Faraday Soc.* (in press).

example, in O_2 in its ground state being paramagnetic), it would be expected to have one electron in each of these p orbitals, i.e. to have a triplet ground state. If CH_2 used pure p C valencies then it would contain a lone pair of $2s$ electrons and have a singlet ground state. The fact that the observed angle (accepting the identification of the 4050 A. bands) is considerably nearer to 180° than to 90° may be held to make it at least possible that the ground state of CH_2 is a triplet and not a singlet.

Such a conclusion would explain the fact that systems containing free CH_3 radicals seem only to give rise to CH_2 with some difficulty. The energy required for the reaction $CH_3 = CH_2 + H$ would be $\approx 105 - 2(115 - 105) = 85$ kcal./mole, so that the activation energy for this reaction would be at least equal to this amount. Further, the reaction $CH_2 = CH + H$ would require $\approx 115 + (115 - 80) - 65 = 85$ kcal./mole if we include the value of 65 (from the work of Long and Norrish) because of the change from a configuration based essentially on tetravalent C to one based on divalent C. Since $CH_4 = CH_3 + H$ requires 101 and $CH = C + H$ requires 80 kcal./mole, we reach a conclusion which has previously been advocated by Voge,[21, 28] namely that the energy required for the successive removal of H atoms in methane (especially after the first) does not vary by any large amount. This conclusion would *not* follow (accepting our other figures) if we included the 65 kcal. at the step $CH_3 = CH_2 + H$, i.e. if we assumed CH_2 to have a singlet ground state.

Finally it is satisfactory that $E(CH)_{CH_2} = 115$ kcal. is consistent with the Long and Norrish value for the energy hurdle: the gain in energy on passing from CH_2 based on diatomic carbon (assumed, by analogy with CH, to employ nearly pure p C valencies) to CH_2 based on tetravalent carbon is $\approx 2 \times (115 - 80) = 70$, which is more than the 65 kcal. to be absorbed. These figures suggest that the singlet and triplet states are very close. The gain of energy on hybridising the carbon valencies in the CH radical (~ 35 kcal.) is of course much less than the hurdle that would have to be surmounted.

The experimental data for CH_2 are not sufficient for certainty in theoretical conclusions, but the above discussion points one way in which the data *can* be used when they become available.

The author would like to acknowledge warmly the debt he owes to C. A. Coulson.

Summary.

The properties of bonds involving carbon are correlated with the degree of hybridisation in the carbon valency employed. This approach translates into other language the approach in terms of electronegativities and polar character which the author has previously employed. The more s character in a carbon valency the more electronegative is the carbon atom in that valency. Using the known relation between electronegativities of bonded groups and bond strength, it follows that the more s character in a carbon valency the stronger the bond to a given atom formed by that valency. The relative strengths of many carbon bonds are thereby explained. The corollary, that the more electronegative an atom (X) joined to carbon the more p character it evokes in the carbon valency to which X is attached, is used to indicate further facts concerning bond strengths and molecular shapes. Particular application of these principles is made to the CH and CH_2 and CH_3 radicals.

Résumé.

Les propriétés de liaisons comportant C sont reliées au degré d'hybridation de la valence employée de C. Plus la valence C a le caractère s, plus l'atome C est électronégatif et plus est forte la liaison, formée par cette valence avec un atome donné. Ces principes sont appliqués aux radicaux CH, CH_2 et CH_3.

[28] Baughan, *Nature*, 1941, 147, 542.

Zusammenfassung

Die Eigenschaften von Bindungen, an denen ein C-Atom beteiligt ist, konnen mit dem Grad der Hybridisierung der entsprechenden C-Valenz in Zusammenhang gebracht werden. Je mehr *s*-Charakter die Valenz besitzt, desto mehr elektronegativ ist das betreffende C-Atom und desto starker ist die durch diese Valenz gebildete Bindung an ein gegebenes Atom. Es folgt eine Anwendung dieser Grundsatze bei CH, CH_2 und CH_3-Radikalen.

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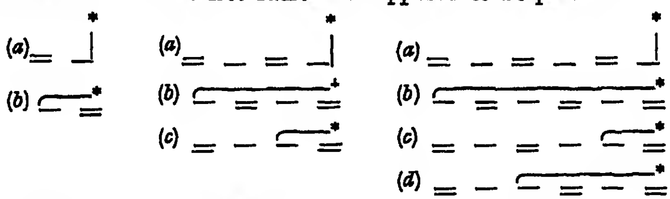
ON THE STUDY OF FREE RADICALS BY THE MOLECULAR-DIAGRAM METHOD.

BY R. DAUDEL.

Received 9th July, 1947.

It has been pointed out that the two methods of constructing molecular diagrams [1] lead to very similar results. To compare these two processes P. and R. Daudel and C. A. Coulson [1] chose the case of polynuclear hydrocarbons. Here we should like to study the case of some free radicals.

We have calculated the mesomeric molecular diagrams [2] of the three radicals C_3H_5, C_5H_7, C_7H_9, in order to compare them with the molecular-orbital diagrams obtained by Coulson.[3] We have made only very simple calculations using the three following sets of canonical structures to describe the free radicals under consideration. As usual [4] the star * denotes a phantom orbit and electron at infinity with which the otherwise unpaired electron of the free radical is supposed to be paired.



C_3H_5 C_5H_7 C_7H_9

In the table below the results obtained are shown diagrammatically

Radical.	Molecular-Orbital Diagram.	Mesomeric Molecular Diagram.
C_3H_5	0·93 0·22 0·93 0·71 0·71	0·50 0·00 0·50 0·50 0·50
C_5H_7	0·85 0·27 0·43 0·27 0·85 0·79 0·58 0·58 0·79	0·37 0·00 0·26 0·00 0·37 0·63 0·37 0·37 0·63
C_7H_9	0·82 0·27 0·43 0·33 0·43 0·27 0·82 0·81 0·55 0·65 0·65 0·55 0·81	0·29 0·00 0·21 0·10 0·21 0·00 0·29 0·71 0·29 0·50 0·50 0·29 0·71

[1] Coulson, Daudel and Daudel, *Revue Sci.*, 1947, **85**, 29.
[2] Daudel and Pullman, *Compt. rend.*, 1945, **220**, 599, 888; 1945, **221**, 201, 247, 298; 1946, **222**, 86, 188.
[3] Coulson, *Trans. Faraday Soc.*, 1946, **42**, 265.
[4] Pauling, *J. Chem. Physics*, 1933, **1**, 280.

and compared with Coulson's diagrams. In the molecular-orbital diagrams on the left the number on an arrow attached to any carbon atom denotes the free valence at that atom, and the number along the bond denotes the mobile bond order. In the mesomeric molecular diagrams on the right, the corresponding quantities are the *indice de valence libre* and the *indice de liaison.*[1]

The agreement between the two methods is very good. It is probable that it would be better if we had introduced the polyexcited structures. However, it is easy to see that the two methods lead to the same general results.

In particular we can say that:

(i) there is a great difference between the classical formulæ and the quantum diagrams;

(ii) the longer the chain the more significant are the fluctuations of the *indice de liaison* from one bond to another;

(iii) on the contrary, the fluctuations of the *indice de valence libre* become smaller;

(iv) the more reactive parts of a radical are its two ends, because they possess the greatest *indice de liaison* and the greatest *indice de valence libre;*

(v) this *indice de valence libre* decreases when the number of π electrons increases. On the other hand the *indice de liaison* increases with this number.

All these general results may be seen also on the molecular-orbital diagrams. A comparison soon shows how good is the agreement between the two methods.

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THE ELECTRONIC STRUCTURE OF SOME FREE RADICALS.

BY MDE. ALBERTE PULLMAN.

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Three stages may be distinguished in the quantum-mechanical investigation of free radicals. The first one, which followed immediately the creation of quantum-mechanical methods of studying organic molecules, was mostly occupied with the determination of the reasons of stability of free radicals. Both the molecular-orbital method and the electron-pair method led to similar conclusions explaining the stability of free radicals by the formation of additional structures, the resonance among which stabilises the molecule by an extra "free-radical resonance energy".[1] The calculation of this free-radical resonance energy carried out by these two methods[2] gave a satisfactory account of the relative stabilities of a large number of free radicals, though in some cases supplementary steric effects were admitted. Some recent calculations[3] complete the list of resonance energies established before.

[1] Previously, a somewhat similar qualitative treatment of the question has been given by Burton and Ingold (*Proc. Leeds Phil. Soc.*, 1929, 1, 421) and by Ingold (*Trans. Faraday Soc.*, 1934, 30, 52) who tried to explain the relative stabilities of the free radicals in terms of "degenerescence of a great number of tautomeric forms."

[2] Hückel, *Z. Physik*, 1933, 83, 632; *Trans. Faraday Soc.*, 1934, 30, 40. Pauling and Wheland, *J. Chem. Physics*, 1933, 1, 370; 1934, 2, 482. Wheland, *ibid.*, 1934, 2, 474.

[3] Wheland, *J. Amer. Chem. Soc.*, 1941, 63, 2025. Syrkin and Diatkina, *Acta Physicochim.*, 1946, 21, 641.

In the second stage of the investigation attention has been drawn to other structural features of free radicals, mostly to the bond order and to the bond length of the different C—C links. By means of the molecular-orbital method, Coulson has evaluated [4] the length of the links in linear free radicals of general formula $C_{2n+1}H_{2n+3}$, and Penney and Kynch have given [5] the internuclear distances in the phenyl-methyl radical, estimated by means of the electron-pair method with the use of Penney's definition of bond order.

Finally, the third stage of this study, which started just a short time ago, is directed towards the determination of the electronic constitution of free radicals. New notions have been introduced both in the molecular-orbital method [6] and in the electron-pair method [7] which are particularly valuable for the interpretation of the chemical behaviour of molecules. Coulson [6] has employed his concept of free-valence number for the study of the configuration and reactivity of the homologous series of linear free radicals $C_{2n+1}H_{2n+3}$. In this paper we want to examine the same series of linear radicals from the electron-pair method point of view and to extend the study to aromatic free radicals.

The Method of Calculation.

The method employed is that established by R. Daudel and A. Pullman,[7] account being taken of the definitions introduced by P. Daudel.[8] The values which have been ascribed previously to the Svartholm's *zones de liaison* and *zones de sommet* are here considered as representing respectively twice the bond order of the total C—C link, and the free-valence number of the carbon atom under consideration. These definitions are adopted here for the sake of their analogy with those employed by Coulson. Otherwise they represent evidently in different terms the same quantities as those which have been used previously by R. Daudel and A. Pullman, i.e. respectively the quantity of coupled electrons located upon a given link and the quantity of free electrons in the neighbourhood of a given carbon atom.

It should also be stated that the bond order as defined by P. Daudel, being the same as that introduced by Pauling, Brockway and Beach,[9] suffers from all the drawbacks of the latter and especially from those which have been pointed out by Penney.[10] In the present paper stress will be laid essentially upon the free-valence numbers which are the more important quantities in the determination of the chemical features of molecules.

Linear Free Radicals of the General Formula $C_{2n+1}H_{2n+3}$.

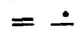
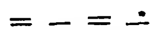
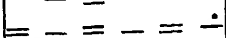
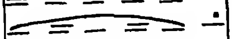
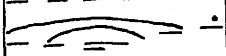
In order to have a good basis for the comparison of our diagrams with those of Coulson we have calculated the electronic configuration of the linear free radicals C_3H_5, C_5H_7, C_7H_9, taking into account all the possible structures for C_3H_5 and C_5H_7 and the two classes of unexcited and singly-excited structures for C_7H_9. The two doubly-excited structures neglected in the case of C_7H_9 are undoubtedly of very little importance. Table I contains the data concerning the relative importance of the different classes of structures, all the formulæ of a given class being considered as equally important. The method employed for the establishment of the secular equation is that of Pauling * introducing a phantom electron.

[4] Coulson, *Proc. Roy. Soc. A*, 1938, **164**, 383.
[5] Penney and Kynch, *ibid.*, 409.
[6] Coulson, *Trans. Faraday Soc.*, 1946, **42**, 106, 265.
[7] R. Daudel and A. Pullman, *Compt. rend.*, 1946, **222**, 663 ; *J. Physique*, 1946, **7**, 59, 74, 105.
[8] P. Daudel, *Compt. rend.*, 1946, **223**, 947.
[9] Pauling, Brockway and Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2705.
[10] Penney, *Proc. Roy. Soc. A*, 1937, **158**, 306.
* *J. Chem. Physics*, 1933, **1**, 280.

The corresponding molecular diagrams are listed in Fig. 1, the numbers placed upon the C—C links indicating the bond order of the link and the numbers placed upon the C atoms indicating the free valence of the atom.

Table II contains a representation of the evolution of the most important features of the configuration of the linear free radicals as a function of the

TABLE I.

Free Radical.	Class of Formulæ.	Type of Formulæ.*	Number.	Importance in %.
C_3H_5	Unexcited		2	100
C_5H_7	Unexcited		3	95
	Singly excited		2	5
C_7H_9	Unexcited		4	90·4
	Singly excited		8	9·6
	Doubly excited		2	neglected

length of the link; the results are in excellent agreement with those obtained by Coulson.

In the course of the preparation of the present paper Mr. Daudel has informed us that he has also constructed molecular diagrams of the above radicals, taking into account only the unexcited structures; and that

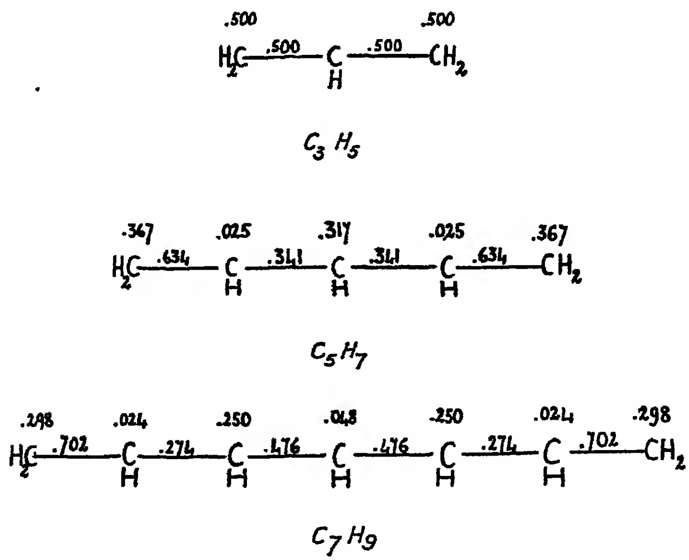


FIG. 1.

already in this approximation the general agreement with Coulson's diagrams was satisfactory. The introduction of the excited structures enables the agreement to be somewhat better, especially by introducing a free-valence number upon all the C atoms.

It should be noted that the most important features of the structure of these free radicals, such as the particular concentration of free valence

* The sign . indicates the position of the odd electron.

at the end-atoms and its decrease with the increasing length of the chain, the high bond order of the end-links and the general tendency of the molecule to uniformise as the chain lengthens, are similar to those found by B. Pullman [11] in the linear unsaturated hydrocarbons $C_{2n}H_{2n+2}$. The presence of the odd electron in the free radicals of course causes the free-valence numbers of these molecules to be much higher than those of the conjugated systems.

The resonance energies of the free radicals calculated in the present

TABLE II.

Free Radical.	The Greatest Free-Valence Number.	The Mean Free-Valence Number.	The Greatest Bond Order.	The Mean Bond Order.
C_3H_5	0·5	0·333	0·5	0·5
C_5H_7	0·367	0·220	0·633	0·487
C_7H_9	0·298	0·177	0·702	0·484

work are as follows: 0·5α for C_3H_5, 0·855α for C_5H_7, and 1·165α for C_7H_9, α being Pauling's usual exchange integral.

Aromatic Free Radicals.

A. General Structure.

The molecular diagrams of this class of free radicals have been constructed by taking into account only the unexcited structures whose coefficients in the molecular wave function have been calculated by Pauling and Wheland.[3] Table III gives the relative importance in %₀ of the different formulæ deduced from the data given by these authors. (The types of the formulæ are those indicated by Pauling and Wheland.)

The fact that the molecular diagrams of the aromatic free radicals have been built up by taking into account only the unexcited structures implies that, although they give a general idea of the constitution of these molecules, they cannot be used for a direct comparison of all the molecules among themselves. The differences in the relative importances of the excited structures must be quite great between, let us say, the biphenylmethyl and a naphthylmethyl * and their introduction would surely modify the comparative features of these two free radicals.† But nevertheless the free radicals studied here may be divided into a few groups and within them a useful comparison may be drawn between the different molecules.

It is easily shown that the comparative study may be done essentially in two cases: (1) in the case of free radicals containing the same aromatic nucleus and differing only in the position of the attached methyl group, (2) in the case of free radicals containing different numbers of the same nuclei.

The corresponding molecular diagrams are listed in Fig. 2, the significance of the numbers being the same as in Fig. 1.

[11] B. Pullman, *Compt. rend.*, 1947, **225**, 61.

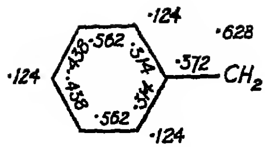
* That this is the case may be seen from the marked differences in the relative importances of different classes of structures in naphthalene (as evaluated by Sherman, *J. Chem. Physics*, 1934, **2**, 488) and in biphenyl (as evaluated by B. Pullman, *Compt. rend.*, 1946, **222**, 1106).

† It may be pointed out that the resonance energies which are not modified greatly by the introduction of excited structures do not suffer from this handicap.

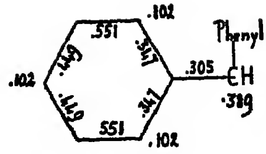
TABLE III.

Free Radical.	The Type of the Formula. The Place of the Odd Electron.	Number of Formulæ.	Importance %.
Phenylmethyl *	methyl group	2	62·8
	phenyl ,,	3	37·2
Biphenylmethyl	methyl ,,	4	58·6
	biphenyl ,,	9	41·4
β-Naphthylmethyl	methyl ,, (symm. napht.)	1	23·1
	methyl group (unsymm. napht.)	2	35·7
	naphthyl group	6	41·2
α-Naphthylmethyl	methyl group (symm. napht.)	1	20·0
	methyl group (unsymm. napht.)	2	31·1
	naphthyl group	7	48·9
Fluoryl	methyl group	4	43·8
	biphenylene-1	8	40·1
	biphenylene-2	4	16·1
Diphenylmethyl	methyl group	4	38·9
	phenyl ,,	12	61·1
Phenylfluoryl	methyl ,,	8	23·0
	phenyl ,,	12	27·9
	biphenylene group	24	49·1
Biphenyldiphenylmethyl	methyl group	16	21·1
	phenyl group	48	49·8
	biphenyl ,,	36	29·1
Triphenylmethyl	methyl ,,	8	19·6
	phenyl ,, (*para* position)	12	22·9
	phenyl group (*ortho* position)	24	57·5
Phenyldibiphenylmethyl	methyl group	32	22·1
	phenyl ,,	48	23·6
	biphenyl ,,	144	54·3
Tribiphenylmethyl	methyl ,,	64	23·2
	biphenyl ,,	432	76·8
β-Naphthyldiphenylmethyl	methyl ,,	12	20·3
	phenyl ,,	36	50·4
	naphthyl ,,	24	29·3
α-Naphthyldiphenylmethyl	methyl ,,	12	18·2
	phenyl ,,	36	46·4
	naphthyl ,,	28	35·4

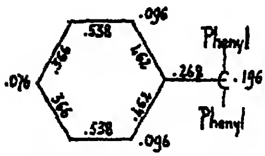
* There is a numerical error in Pauling and Wheland's calculations of the coefficients of the two groups of formulæ in the wave function of this free radical, which is not included in the general erratum given by this author (*J. Chem. Physics*, 1934, **2**, 482); the ratio of the coefficients of the two groups of formulæ should be 1 : 0·626 instead of 1 : 1·0279. We are indebted to Prof. Coulson for having suggested, from the general aspect of his own (m.o.) diagrams of mono-, di- and tri-phenylmethyl radicals (see this Discussion) the existence of this error. The values given in this table are the corrected ones.



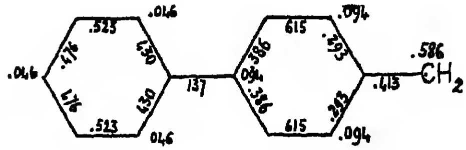
I Phenylmethyl.



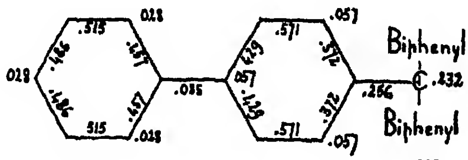
II. Diphenylmethyl.



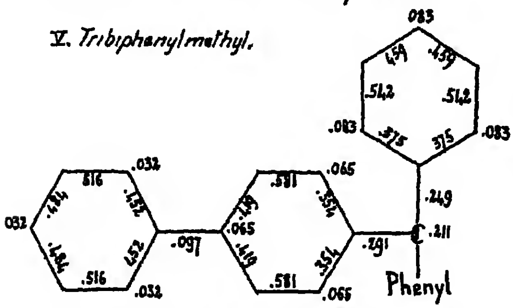
III. Triphenylmethyl.



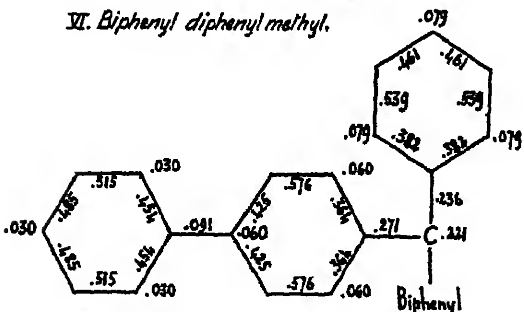
IV. Biphenylmethyl.



V. Tribiphenylmethyl.

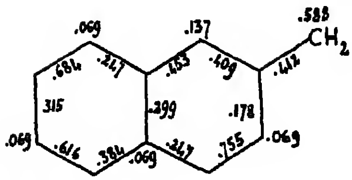


VI. Biphenyl diphenyl methyl.

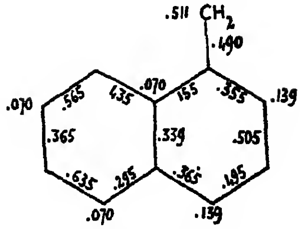


VII. Phenyl dibiphenylmethyl.

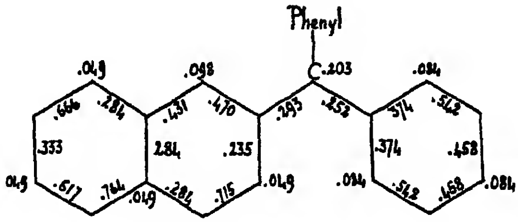
FIG. 2.



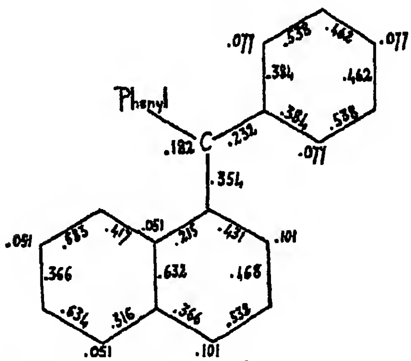
VIII β-naphtylmethyl.



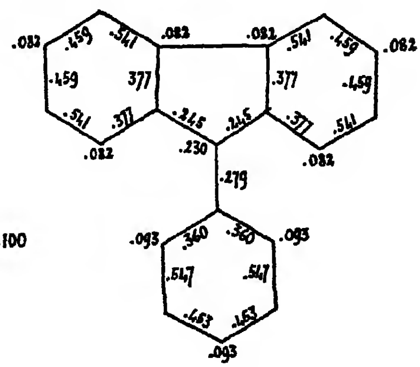
IX. α-naphtymethyl.

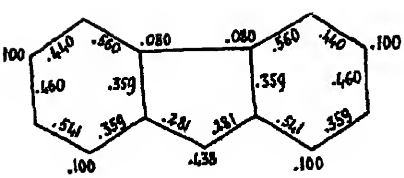


X. β-naphtyl diphenylmethyl.



XI α-naphthyl diphenylmethyl.





XII. Fluoryl.

XIII. Phenylfluoryl.

Fig. 2

B. A Comparative Study of some Groups.

(1) β-NAPHTHYLMETHYL, α-NAPHTHYLMETHYL.—This comparison leads to the same results as those which would be obtained in comparing β- and α-substituted naphthalenes, carrying at these positions an electron-donating group. The relative values and the distribution of the free valence in the naphthalene nucleus are those which would be predicted by the application of our method of evaluating the influence of substituents upon the electronic structure of aromatic molecules [12] and by the application of the general rules given by B. Pullman.[13] Namely, the highest concentration of the free valence on the nucleus is located at the 2- and 4-positions of the α-naphthylmethyl and at the 1-position of the β-naphthylmethyl. The total electron loss of the methyl group, measuring the degree of conjugation of the free electron, is greater for the α-position than for the β-position and consequently the bond order of the link $C_{meth.}$—$C_{arom.}$ is greater in the α-naphthylmethyl than in the β-naphthylmethyl. In this case, as in others which are well suited for a comparative study, the order of the aryl hydrocarbon groups in promoting radical stability as determined by the values of the extra free-radical resonance energy goes parallel with the order of increasing conjugation as determined by the diminution of the free-valence number of the methyl group.*

TABLE IV.—THE MOST OUTSTANDING FEATURES OF THE STRUCTURE OF THE AROMATIC FREE RADICALS REPRESENTED IN A CONCISE WAY.

Free Radical.	Decrease below Unity of the f.v.n. of the Meth. gr.	F.v.n. of the Rest of mol. Greatest.	F.v.n. of the Rest of mol. Mean.	Bond Order of $C_{meth.}$—$C_{arom.}$	The Highest Bond Order of the rest of mol.
Phenylmethyl	0·372	0·124	0·124	0·372	0·562
Biphenylmethyl	0·414	0·094	0·070	0·414	0·614
β-Naphthylmethyl	0·412	0·137	0·082	0·412	0·754
α-Naphthylmethyl	0·489	0·139	0·098	0·489	0·635
Fluoryl	0·562	0·100	0·093	—	0·560
Diphenylmethyl	0·611	0·102	0·102	0·305	0·551
Phenylfluoryl	0·770	0·093	0·086	—	0·504
Biphenyldiphenylmethyl	0·789	0·083	0·065	0·291 0·249	0·581
Triphenylmethyl	0·804	0·096	0·089	0·268	0·538
Phenyldibiphenylmethyl	0·779	0·079	0·052	0·236 0·271	0·576
Tribiphenylmethyl	0·768	0·057	0·042	0·256	0·571
β-Naphthyldiphenylmethyl	0·797	0·098	0·073	0·293 0·252	0·715
α-Naphthyldiphenylmethyl	0·818	0·101	0·074	0·354 0·232	0·633

The results obtained in the case of β-naphthylmethyl and α-naphthylmethyl may be extended to higher aryl groups and it can easily be shown that for a given aryl group (and if steric effects are neglected) the conjugation power of the odd electron and the stabilising power of the group

[12] A. Pullman, *Ann. Chim.*, 1947, **2**, 1.

[13] B. Pullman, *Compt. rend.*, 1946, **222**, 1396.

* This comparison may include the phenylmethyl radical. This has not been done directly as the results have been somewhat obscured by the numerical error explained before. When this is done it can easily be seen that in agreement with B. Pullman's general rules [13] of which the principal states that *the power of conjugation of a given substituent is proportional to the free valence of the carbon atom carrying it*, the degree of conjugation of the odd electron is greater in the naphthylmethyl radicals than in phenylmethyl. (F.v. equals 0·073 in benzene, 0·098 for a C atom in the β position and 0·122 for a C atom in the α position in naphthalene.) Another of these rules which states that the mean perturbation of the free valence of the hydrocarbon, produced by a substituent, decreases with the increase in the size of the molecule carrying it, is also verified.

are the highest when the methyl group is attached to the carbon atom, which had the greatest free-valence number in the unsubstituted molecule; e.g. 9-anthryl should be better in promoting radical stability than 1-anthryl which in turn should be better than 2-anthryl.

(2) PHENYLMETHYL, DIPHENYLMETHYL, TRIPHENYLMETHYL.—The essential points resulting from this comparison are:

(*a*) the steady decrease in the free-valence number of the methyl group on the adjunction of a new phenyl group:

(*b*) the steady decrease, as the number of the phenyl groups increases, of the free-valence numbers of the phenyl carbons;

(*c*) the steady decrease, in the same conditions, of the bond order of the $C_{meth.}$ —$C_{arom.}$ link;

(*d*) it should be noted that the differentiation, in the case of triphenylmethyl, between the weights of the structures containing the odd electron at the *ortho*- or *para*-positions of the phenyl groups indicates a higher concentration of free valence at the *ortho*-positions. This is probably a general case and should be compared with the results obtained recently by B. Pullman in the study of the electronic configuration of polyphenylethylenes and polyphenylbenzenes.[14]

(3) BIPHENYLMETHYL, TRIBIPHENYLMETHYL.—It is easily observed that there is a marked diminution in the residual free valence of the methyl group on the adjunction of a new biphenyl group. As the number of perturbed biphenyl carbons increases rapidly, there is a steady decrease in the free-valence numbers of these atoms in spite of the increasing conjugation of the odd electron. In all cases the values of the free-valence numbers of the atoms belonging to the nucleus adjacent to the methyl group are higher than those of the other nucleus.

(4) The remaining groups such as β-naphthyldiphenylmethyl, α-naphthyldiphenylmethyl and biphenyldiphenylmethyl, phenyldibiphenylmethyl may also be compared, but in these cases some important modifications may perhaps be introduced if the excited structures were taken into account.

(5) A particular group is formed by the fluoryl and phenylfluoryl radicals. The adjunction of a phenyl group produces a strong increase in the conjugation power of the odd electron and consequently a decrease in the residual free-valence number of the methyl group. The mean free-valence number of the fluoryl nucleus has also decreased. In connection with this it may be observed that the degree of conjugation of the odd electron in fluoryl may be compared with that of the odd electron in other free radicals containing the same total number of electrons, e.g. in diphenylmethyl and biphenylmethyl. It is seen then that the decrease (from unity) of the free-valence number of the methyl group is highest in the most stable of these radicals (diphenylmethyl) and the lowest in the less stable (biphenylmethyl).

C. The Importance of the Singly-excited Structures.

In order to have an idea about the approximate importance of the neglected excited structures we have also calculated the molecular diagram of phenylmethyl, taking into account besides the structures considered by Pauling and Wheland also the five singly-excited structures containing the ineffective link inside the benzene nucleus. On considering, as a first approximation, that the unexcited structures on the one hand and the singly-excited on the other are equally important among themselves, we obtain for the relative weights of these two groups of structures, 85 °/₀ for the unexcited structures and 15 °/₀ for the excited ones. This is probably the order of magnitude of the error committed by neglecting the excited structures in this particular case and the error is undoubtedly greater

[14] B Pullman, *Compt. rend.*, 1947, 224, 1773.

for bigger molecules. It is interesting to note that it seems that the error is of the same order of magnitude as that committed by neglecting the excited structures in the corresponding hydrocarbons.

The molecular diagram of phenylmethyl constructed with these new data is represented in Fig. 3. It may be seen that though the absolute values of the free valence and bond order distribution are modified this does not change the general conclusions reached before.

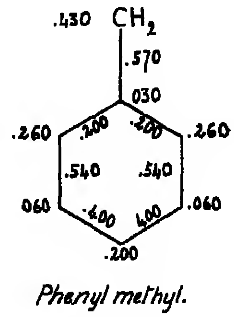


FIG. 3.

Conclusions.

In conclusion it may be stated that the general aspect of the molecular diagrams of the free radicals explains the particular reactivity of these molecules, in the same way as the molecular diagrams of polycyclic hydro-carbons gave a satisfactory account of their behaviour.[7, 12] The free valence, though it seems to be widely spread over the whole molecule, remains nevertheless strongly concentrated at the methyl group, which should form a centre of a particularly high reactivity. That it is so, may be seen from the well-known reactions of the free radicals. We shall not enumerate them in detail as a full account of them may be found in any modern treatise of organic chemistry.[15] Let us, however, mention, for the typical example of triphenylmethyl, some of the most common ones such as easy fixation of halogens to give $(C_6H_5)_3C$—Hal., fixation of alkali metals to give $(C_6H_5)_3CM$, of hydrogen to give triphenylmethane, of oxygen to give a peroxide $(C_6H_5)_3C—O_2—C(C_6H_5)_3$, etc.

Résumé.

La méthode des diagrammes moléculaires de R. Daudel et A. Pullman est employée pour déterminer la distribution de l'indice de valence libre et de l'indice de liaison dans les radicaux libres linéaires et aromatiques. Les résultats concernant les radicaux libres linéaires sont en accord avec ceux obtenus par Coulson à l'aide de la méthode des orbites moléculaires. On donne une étude comparative des différentes classes de radicaux aromatiques et on montre que les diagrammes électroniques ainsi obtenus rendent bien compte de la réactivité particulière des molécules étudiées.

Zusammenfassung.

Die Methode der molekularen Diagramme von R. Daudel und A. Pullmann wird zur Bestimmung der Verteilung des "Indexes der freien Valenz" und der Bindungsordnung in geradlinigen und aromatischen freien Radikalen benützt. Für geradlinige freie Radikale stehen die Ergebnisse mit den nach der Methode der molekularen Elektronenbahnen von Coulson erhaltenen im Einklang. Die verschiedenen Klassen von aromatischen Radikalen werden vergleichsweise untersucht. Die so erhaltenen Elektronendiagramme stimmen gut mit der speziellen Reaktivität des untersuchten Moleküls überein.

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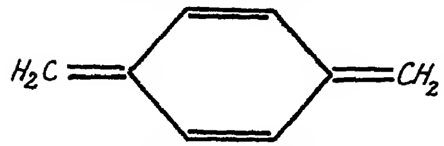
[15] e.g. Pascal, *Traité de Chimie Organique de Grignard et Baud*, Tome 2, p. 761. Bachman, *Organic Chemistry* (Gilman), Vol. I, p. 589.

p-QUINODIMETHANE AND ITS DIRADICAL.

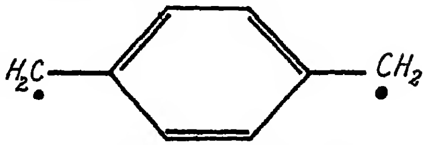
By C. A. Coulson, D. P. Craig, Allan Maccoll and Mde. A. Pullman.

Received 6th October, 1947.

p-Quinodimethane (I) and its diradical (II) have been proposed by Szwarc [1] as products in the pyrolysis of p-xylene:



p-Quinodimethane.
I.

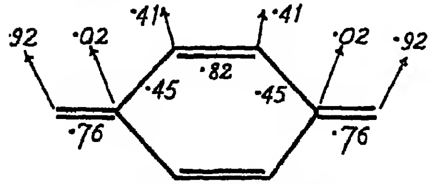


p-Quinodimethane di-radical.
II.

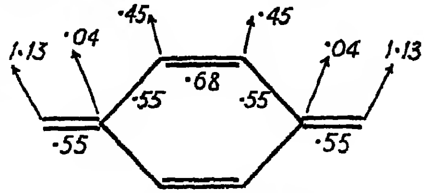
In the following we report calculations of energies, bond orders, and free valences in these structures.

Molecular-Orbital Treatment.—The method of molecular orbitals has been described in an earlier paper in this Discussion.[2] In the ground state of the molecule (I), which is a singlet state, the resonance energy is $1{\cdot}93\beta$, in agreement with the value previously found by Namiot, Diatkina and Syrkin.[3] The value is nearly as large as in benzene (2β) indicating a high stability, as found by Szwarc in the gas phase. The mobile bond orders and free valences are shown in (III). The free valences in the ring itself are very similar to those found in more normal molecules, like diphenyl or benzyl. But the free valence at the end carbons is much larger than is usually found except for free radicals. Thus in benzyl[2] the end value is 1·04, only slightly greater than in our present molecule. Hence the reactivity of this molecule ought to be high at both ends, under conditions where close contact obtains. This explains why the molecule is very labile in the liquid phase.

Szwarc has suggested that the molecule is originally formed as the biradical (II). This would be a triplet, whose energy calculated in the way suggested by Diatkina and Syrkin [4] by identifying the triplet state as the first excited one and neglecting the difference between excited singlet and triplet, exceeds that of the ground state by about $0{\cdot}62\beta$, or 12 kcal. It is probable (C. A. Coulson, unpublished calculations on the singlet-triplet separations in excited states) that the true value is somewhat less than this, perhaps 8 or 9 kcal. The bond orders and free valences in this excited state are shown in (IV). The free valences in this treatment differ surprisingly little from those in the ground state. The triplet



Ground state (singlet).
III.



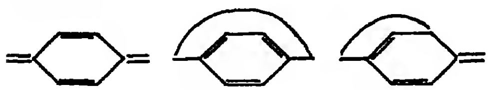
Excited state (triplet).
IV.

[1] Szwarc, this Discussion, p. 46.
[2] Coulson, this Discussion, p. 9.
[3] Namiot, Diatkina and Syrkin, *Compt. rend., U.R.S.S.*, 1945, 48, 233.
[4] Diatkina and Syrkin, *Acta Physicochim.*, 1946, 21, 23.

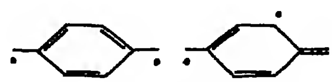
excited state would not therefore be expected to be much more reactive than the singlet ground state, with normal benzyl lying half-way between the two.

Valence-Bond Treatment.—Using the valence-bond method, Syrkin and co-workers [3] find the resonance energy of quinodimethane (I) to be $1{\cdot}05\alpha$, or about 38 kcal. This value compares well with the molecular-orbital value of $1{\cdot}93\beta$, giving the usual value 0·55 for the ratio β/α. With structures of the types shown in (V) (a slightly less complete set than that of Namiot, Diatkina and Syrkin), the energies of the ground and first excited states are $Q + 2{\cdot}905\alpha$ and $Q + 0{\cdot}199\alpha$, leading to a ground-state resonance energy of $0{\cdot}905\alpha$ and a transition energy of $2{\cdot}706\alpha$. The predicted long-wave absorption band (a forbidden transition) would lie at about 2360 A. The compound should thus absorb in the ultraviolet.

For the triplet (biradical) state structures of the types shown in (VI) were used:



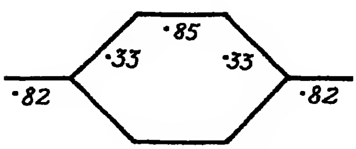
Singlet structure types.
V.



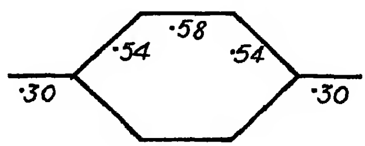
Triplet structure types.
VI

The lowest triplet level is at $Q + 1{\cdot}88\alpha$. Thus the separation between lowest singlet and lowest triplet is about 45 kcal., a value very much greater than that from the molecular-orbital treatment. The resonance energy of the triplet state (relative to a single triplet structure) is $1{\cdot}38\alpha$, or about 49 kcal. It appears that there would be a negligibly small concentration of diradicals in equilibrium with molecules at room temperature.

Calculations of bond order, using the definition of Penney,[5] are shown for the molecule (VII) and the diradical (VIII). These are to be compared with (III) and (IV) respectively. The comparison appears satisfactory when the different definitions of bond order in the two cases are noted.



Singlet state.
VII.



Triplet state.
VIII.

There is no justification in the literature for the use of $\alpha = 1{\cdot}92$ e.v. in valence-bond resonance-energy calculations, as has been done by Szwarc in connection with the resonance energy of the benzyl radical. On the evidence at present available the value $\alpha = 1{\cdot}4$ or $1{\cdot}5$ e.v. is indicated for the calculation of resonance energies, and the value 1·92 e.v. for the calculation of energy-level separations (transition energies or singlet-triplet separations). It is possible, however, that a different value still will prove to be appropriate to the discussion of free radicals. The values above are those used in the present calculations.

Another point in Szwarc's paper to which attention may be drawn is the following. The high reactivity of large aromatic molecules, such as rubrene and pentacene, which has been taken by some people as an argument in favour of their biradical structure can easily be interpreted, in the usual language of v.b. molecular-diagrams method, by saying that these molecules present a particularly high concentration of free valence at the carbon atoms at fused rings. In a recent paper [6] curves are drawn

[5] Penney, *Proc. Roy. Soc. A*, 1937, **158**, 306.
[6] Pullman, *Ann. Chim.*, 1947, **2**, 5.

which effectively show that there is a steady increase in the mean and maximum free valence of aromatic molecules with increasing number of condensed benzene nuclei. It can also be shown that in the series of linear polynuclear hydrocarbons the polarisability of the molecules to approaching reagents becomes easier when the chain lengthens,[7] which also accounts quite well for the great reactivity of the above large molecules.

Two of us (D. P. C. and A. M.) wish to acknowledge tenure respectively of Turner and Newall and I.C.I. Fellowships in the University of London.

Summary.

Calculations of energy, bond order, and free valence are reported for the molecule and diradical *p*-quinodimethane. Both the molecular-orbital and valence-bond methods are used. The resonance energy of the molecule is the same in both methods, namely 38 kcal. The resonance energy of the triplet (diradical) quinodimethane is 49 kcal. in the valence-bond treatment. The separation between ground-state singlet and lowest triplet state is much greater in the valence-bond treatment (45 kcal.) than in the molecular orbital (9 kcal.). In either case however there would be a negligible concentration of radicals in equilibrium with molecules at room temperature. The molecule has an unusually large free valence on the terminal carbon atoms. This fact would be associated with a high reactivity at these carbon atoms.

Résumé.

On calcule, à la fois par la méthode des orbites moléculaires et par celle des liaisons de valence, les valeurs de l'énergie, de l'ordre de liaison et de la valence libre pour la molécule et le biradical *p*-quinodiméthane ; pour la molécule, l'énergie de résonance est de 38 kcal. par les deux méthodes, et pour le triplet du biradical, de 49 kcal. par le méthode des paires électroniques. Entre le singulet de l'état normal et l'état le plus bas du triplet, la séparation est de 45 kcal. (méthode des paires électroniques) et 9 kcal. (méthode des orbites moléculaires) ; pour chacune de ces valeurs, la concentration des biradicaux en équilibre avec les molécules à la température ordinaire est négligeable. La molécule a, sur l'atome de C terminal, une valence libre anormalement grande, qui est associée à la haute reactivité de ces atomes de C.

Zusammenfassung.

Berechnungen der Energie, Bindungsordnung und freien Valenz des Moleküls und des Diradikalzustandes von *p*-Chinodimethan werden berichtet. Sowohl die " Methode der molekularen Elektronenbahnen " als auch die " Valenzbindungsmethode " wurden angewendet. Beide Methoden geben den Wert 38 kcal. für die Resonanzenergie des Moleküls. Die Resonanzenergie des Tripletzustands (Diradikal) ist 49 kcal. bei Benützung der Valenzbindungsmethode. Die Energiedifferenz zwischen dem niedrigsten Singletzustand und dem niedrigsten Tripletzustand ist in der Valenzbindungsmethode weit grösser (45 kcal.) als in der Methode der molekularen Elektronenbahnen (9 kcal.), aber aus beiden Resultaten ergibt sich, dass die Anzahl der Radikale, die bei Zimmertemperatur mit Molekülen im Gleichgewicht sind, verschwindend klein ist. Das Molekül besitzt eine ausserordentlich grosse freie Valenz an den Endkohlenstoffatomen, woraus sich eine hohe Reaktivität an diesen Atomen ergeben würde.

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University College, London.

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Paris.

[7] Wheland, *J. Amer. Chem. Soc.*, 1942, 64, 900.

THE RESONANCE ENERGY OF THE BENZYL RADICAL.

By M. Szwarc.

Received 11th August, 1947.

Recent investigation of the pyrolysis of toluene and the xylenes [1] has shown that the resonance energy * of the benzyl radical is 24·5 kcal. This is considerably higher than the generally accepted value as calculated by Pauling and Wheland [2] by the electron-pair bond method, and still higher than that calculated by Hückel,[3] using the molecular-orbital method. The calculations of Pauling and Wheland gave 16 kcal. for the resonance energy of this radical whereas Hückel estimated it as 11 kcal. It would therefore be interesting to review the evidence from other sources in the light of these conflicting values.

Qualitative Evidence.—It has been recognised from experimental data that the benzyl radical possesses great stability; thus, of the more complex organic radicals, it is the only one which has been detected by the Paneth technique. Paneth and Lautch [4] obtained it by the decomposition of $Sn(CH_2 . C_6H_5)_4$ and $C_6H_5CH_2 . CO . CH_2 . C_6H_5$, and also by the reaction between benzyl chloride and sodium atoms. They found its half-life time in hot tubes to be 6×10^{-3} sec. Hein and Mesèe,[5] using a technique similar to that developed by Rice, detected the benzyl radical among the products of pyrolysis of toluene, and were able to identify it in the form of mercury dibenzyl. The above-mentioned authors concluded from their work that the weakest bond in toluene is the C—H bond of the methyl group, and this indicates that the resonance energy of the benzyl radical must be more than 17 kcal.

The stability of the benzyl radical was demonstrated by Horrex and Szwarc,[6] who found that this radical did not combine with oxygen up to 500° C.; moreover, no reaction was detected with either hydrogen, N_2O or NO under similar conditions. During his study of polymerisations initiated by benzyl radicals, Mark [7] came to similar conclusions regarding the non-reactivity of the benzyl radical with oxygen and NO. This high degree of stability of the benzyl radical suggests a high value for its resonance energy; although, of course, it is impossible to draw any quantitative conclusion from these kind of data.

Evidence Concerned with Sodium-Flame Reactions.

Quantitative deductions can be made, however, from the studies of Polanyi and his collaborators conducted in connection with the reactions between the organic halides and sodium atoms. Let us consider the following two reactions:

$$R_1Cl + Na \rightarrow R_1 + NaCl$$
$$R_2Cl + Na \rightarrow R_2 + NaCl$$

for which the energies of activation are E_1 and E_2 respectively. Let us assume that the C—Cl bond energy is B_1 for R_1Cl, and B_2 for R_2Cl. Evans and Polanyi [8] deduced that

$$E_1 - E_2 = -\gamma . (B_1 - B_2) \dagger$$

* Resonance energy of radical = additional resonance energy existing in the radical but not in the undissociated molecule.

† In the original paper H (heat of reaction) is used instead of B. Because in this case $\Delta H = \Delta B$, it is possible to use B instead of H.

[1] Szwarc, *Nature*, 1947, **160**, 403; *J. Chem. Physics*, 1948, **16**, 138.
[2] Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362.
[3] Hückel, *Z. Physik*, 1933, **83**, 632.
[4] Paneth and Lautch, *J. Chem. Soc.*, 1935, 380.
[5] Hein and Mesèe, *Ber. B*, 1943, **76**, 430.
[6] Horrex and Szwarc (to be published).
[7] Private communication of Prof. Herman Mark.
[8] Evans and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1933; *ibid.*, 1938, **34**, 22.

and it was shown by Butler and Polanyi[9] that γ has a value of 0·27 – 0·28. If we assume that the difference $(B_1 - B_2)$ for CH_3Cl and $C_6H_5CH_2Cl$ is equal to the resonance energy of the benzyl radical, we can calculate this quantity from the corresponding energies of activation for the reactions with sodium atoms. The energy of activation for the reaction between sodium atoms and CH_3Cl was measured by Heller and Polanyi[10] and found to be 9·7 kcal. The corresponding reaction with benzyl chloride gave 2·5 kcal. (Evans and Walker[11]) for the energy of activation. Thus we get the resonance energy of the benzyl radical as 26 kcal. This value should be even higher because of the additional resonance energy due to the ionic contribution to the ground state of the molecule,[12] which is greater for benzyl chloride than for methyl chloride.

Let us briefly repeat the method used by Evans and Polanyi to calculate the energy of activation for the reaction between the organic halide and the sodium atom. The transition state was found by the intersection of the Morse curve, representing the energy of the R—Cl bond, with the repulsion curve, corresponding to the system R—Cl⁻, as is shown in Fig. 1.

It must be remembered that the relationship between E and B was obtained by the above-mentioned authors on the assumption that the repulsion curve for

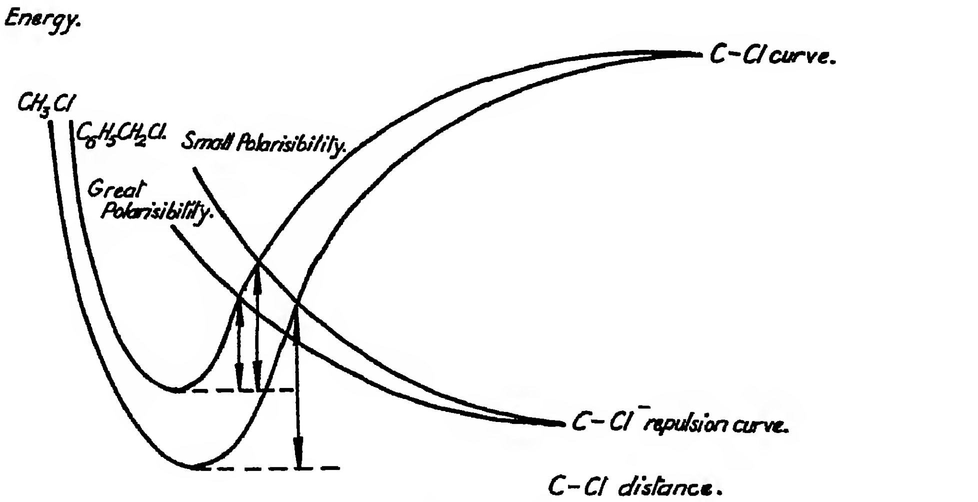


FIG. 1.—Relationship between bond energies and heats of activation in sodium-flame reactions. Arrows represent the heats of activation.

R and Cl⁻ has the same shape for all radicals R. However, it is reasonable to assume that the repulsion curve is flatter if the polarisibility of the R radical is greater.* Therefore the repulsion curve will be flatter for the benzyl radical than for the methyl radical, and this will cause a relatively greater decrease in energy of activation in the reaction between benzyl chloride and sodium atoms than was expected from previous considerations (as is seen from Fig. 1). Thus we conclude that the resonance energy of the benzyl radical, calculated above on the previous assumption, is rather too high.

[9] Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 29.
[10] Heller and Polanyi, *ibid.*, 1936, **32**, 633.
[11] Evans and Walker, *ibid.*, 1944, **40**, 384.
[12] Baughan, Evans and Polanyi, *ibid.*, 1941, **37**, 377.

* The effect of the polarisibility will be specially pronounced in the benzyl radical, where the electron transfer from the C atom of the methyl group to the benzene ring should occur quite easily under the influence of the approaching Cl⁻ ion.

The Value of α.

Let us now turn to the theoretical treatment of the resonance energy of the benzyl radical as worked out by Pauling and Wheland. The treatment of Pauling and Wheland [2] leads to 0·5092 α for this resonance energy, where α is the single exchange integral involving adjacent carbon atoms. They contend that there is considerable evidence for the value $\alpha = 1{\cdot}4$ e.v. (32·2 kcal.), and thus they obtained 16 kcal. for the above-mentioned resonance energy. However, it is possible that the value of α is much higher. For example, Sklar [13] calculated the value of α using Kistiakowsky's data for heat of hydrogenation of benzene and cyclohexadiene, and obtained $\alpha = 1{\cdot}92$ e.v. This value was used by him to calculate the fluorescent spectrum for benzene and other unsaturated hydrocarbons, and gave results in excellent agreement with experimental observations. Assuming Sklar's α-value, we get for the resonance energy of the benzyl radical the value of 22·5 kcal., which is in a fair agreement with that obtained from the study of the pyrolysis of toluene (24·5 kcal.).

The Problem of the C—C Bond in Dibenzyl.

In connection with the resonance energy of the benzyl radical, it is relevant to discuss the problem of the C—C bond energy in dibenzyl. The dissociation of dibenzyl into two benzyl radicals should require $2 \times 24{\cdot}5$ kcal. less energy than the dissociation of ethane into two methyl radicals due to the resonance energy of the benzyl radicals. Assuming the C—C bond energy in ethane to be 85 kcal.,[17] we should expect the C—C bond energy in dibenzyl to be equal to 36 kcal.

It is possible to calculate this bond energy, knowing the heat of formation of toluene (given recently by Prosen, Johnson and Rossini [14] as $-11{\cdot}95$ kcal.), the heat of formation of dibenzyl (estimated by Parks [15] as $-27{\cdot}8$ kcal.) and the bond energy of the C—H bond in toluene (77·5 kcal. from data obtained by the pyrolysis of toluene [1]). Thermochemical calculations based on these data give a value of 47·1 kcal. for the C—C bond in dibenzyl.

The difference of 11 kcal. between these two values for the bond energy of the C—C bond in dibenzyl, we interpret as a strengthening of this bond compared with the pure single C—C bond. This strengthening may be explained in terms of the partial double-bond character of this bond, resulting from the contribution of structure (I) to the ground state of the molecule. The structure (I), due to the hyperconjugation, gives a completely conjugated system.

$$\underset{}{C_6H_5} . \underset{(H)}{CH} = \underset{(H)}{CH} . C_6H_5 \qquad . \quad . \quad . \quad . \quad (1)$$

The above-mentioned partial double-bond character should reveal itself by a shortening of the C—C bond in dibenzyl. The length of this bond was measured by Jeffrey [16] and was found to be 1·48 A.; that is, 0·06 A. shorter than the normal single C—C bond. By means of the relationship between the bond length and the bond energy [17] it is possible to calculate that the shortening of the C—C bond from 1·54 A. to 1·48 A. corresponds to an energy increase of 13·7 kcal. Thus both, the experimental and theoretical approaches, lead to practically the same value for the strengthening of the C—C bond in dibenzyl.

The above relationships are clearly understandable from Fig. 2, which represents the energy curves for the C—C bond in ethane and dibenzyl.

[13] Sklar, *J. Chem. Physics*, 1937, 5, 699.
[14] Prosen, Johnson and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, 36, 455.
[15] Parks *et al.*, *J. Amer. Chem. Soc.*, 1946, 68, 2527.
[16] Jeffrey, *Proc. Roy. Soc., A*, 1947, 188, 222.
[17] Skinner, *Trans. Faraday Soc.*, 1945, 41, 645.

We see that the relationship between the bond length and bond energy is not a simple one, and that it is possible to visualise bonds which are both weaker and shorter than the single bonds from which they are derived. This treatment can be generalised for other systems, and it probably also applies to compounds of the di-allyl class. For one member of this class (geranylamine hydrochloride) Bateman and Jeffrey [18] have reported a shortening of the C—C bond, which is generally held to be a weak one, and envisaged the hyperconjugated structure as a possible explanation of the shortening, and for the co-planar arrangement of the adjacent carbon atoms.

It should be noted that the calculated value of 11 kcal. for the strengthening of the C—C bond in dibenzyl is independent of the particular value chosen for the C—H bond energy in toluene. It is intended therefore, to conduct other experiments to ascertain the strength of the C—C bond in dibenzyl, and thus to provide further data for the calculation of the resonance energy of the benzyl radical.

At any rate it can be seen that the increase in the resonance energy of the appropriate radical can be counterbalanced to some extent by the

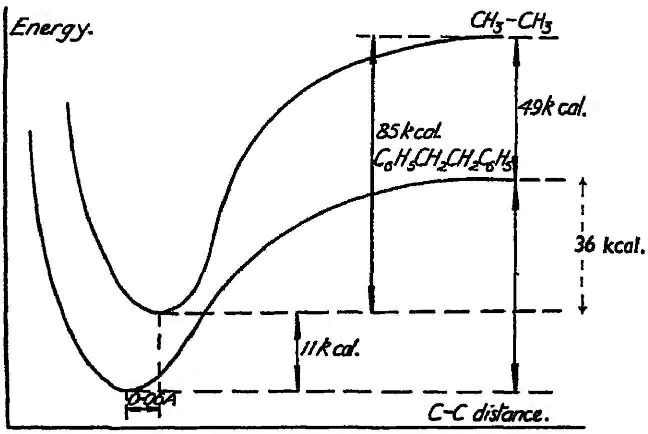


FIG. 2.—Relationship between the bond energy and the bond distance in molecules of ethane and dibenzyl.

increase of the energy of the C—C bond due to hyperconjugation of the type described above. This factor probably explains why *sym*-tetra-*p*-biphenylethane is not dissociated at all, whereas according to the theory based only on the resonance in radical, its dissociation should be appreciable. Therefore, the high resonance energy of the benzyl radical does not imply directly a considerable decrease in the C—C bond energy in tetraphenylethane or in similar compounds.

Triphenylmethyl Radical.

The case of hexaphenylethane is an exceptional one. We cannot expect the resonance energy of the triphenylmethyl radical to be much higher than that of the benzyl radical. The resonating structures in triphenylmethyl, as suggested by Hückel and by Pauling and Wheland, require a planar configuration of this radical. We know from the study of Wallis and Adams [19] on the racemisation of optically active triarylmethylthioglycolic acid that the tervalent carbon atom has a planar

[18] Bateman and Jeffrey, *Nature*, 1942, 152, 446; *J. Chem. Soc.*, 1945, 211.
[19] Wallis and Adams, *J. Amer. Chem. Soc.*, 1933, 55, 3838.

configuration, but this does not imply a coplanar arrangement of the three phenyl groups. It was pointed out to me by Prof. M. Polanyi that such a structure is impossible because of the bulkiness of the phenyl groups, and that the true shape of this radical should be propellor-like.

Fig. 3 represents the coplanar arrangement of the triphenylmethyl radical, and we see that the *ortho* hydrogen atoms are at a distance of 0·76 A. whereas non-bonded hydrogen atoms should at least be at a distance of 2·4 A. (taking the van der Waals radius for hydrogen atoms as 1·2 A.). Therefore the benzene rings must be twisted at least by 30°, bringing the *ortho* hydrogen atoms at least 1·1 A. above the plane determined by the carbon atoms 1, 2, 3 and 4. The lack of coplanarity makes irrelevant the calculations of Pauling and Wheland,[9] which give for the resonance energy of the triphenylmethyl radical a value of 38 kcal. (assuming α = 1·4 e.v.), or a value of 52 kcal. if α = 1·92 kcal.

From the studies of Bent and collaborators [20] it would seem that the resonance energy of the triphenyl methyl radical is rather of the order of

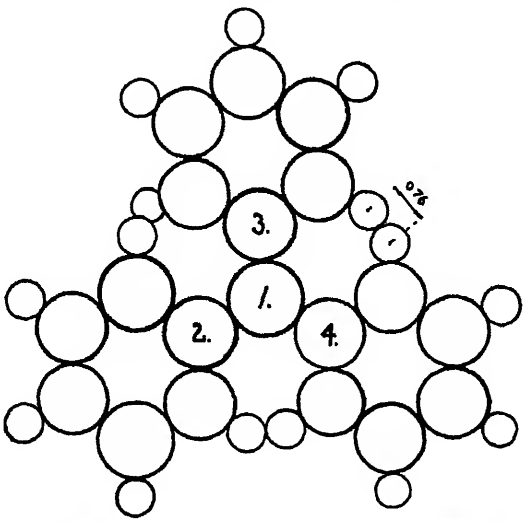


Fig. 3.—The coplanar arrangement of atoms in the triphenyl methyl radical. The circles represent the H and C atoms with the radii corresponding to the covalent radii.

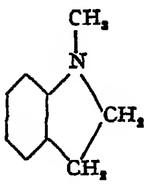
20-25 kcal. Bent and Cuthbertson estimated experimentally the heat of hydrogenation of hexaphenylethane to triphenylmethane, and interpreted their results as an indication of the extra weakening of the C—C bond in hexaphenylethane (to an extent of 27 kcal.), which does not occur in the C—H bond of triphenylmethane. The additional weakening of 47 kcal., which decreases the energy of the C—C bond in that molecule from the normal value of 85 kcal. to the actually-found value of 11 kcal. (Ziegler [21]), was assumed by them to be due to the resonance in the two radicals formed.

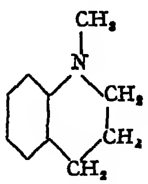
It seems, however, that the contribution of the quinonoid structures is still smaller, and perhaps even quite negligible. From a study of

[20] Bent and Ebers, *J. Amer. Chem. Soc.*, 1935, 57, 1245; Bent, Cuthbertson, Dorfman and Leary, *ibid.*, 1936, 58, 165; Bent and Cuthbertson, *ibid.*, 1936, 58, 170.

[21] Ziegler and Ewald, *Annalen.*, 1929, 473, 163; also Müller and Müller-Rodloff, *ibid.*, 1935, 521, 89; Wooster, *J. Amer. Chem. Soc.*, 1936, 58, 2156; Preckel and Selwood, *ibid.*, 1941, 63, 3397.

Remington,[22] on the effect of steric inhibition on the resonance, we can see that the condition of coplanarity is of the utmost importance. Remington has shown a decrease in the intensity of the adsorption band of dimethylaniline, which is connected with the contribution of the quinonoid structure of the molecule, if a methyl group is added in *ortho* position (but not in *para*). The decrease is very strong if two methyl groups occupy *ortho* positions, and the band practically disappears if the tertiary butyl group is substituted in the *ortho* position of dimethylaniline. Similarly the band exists in compounds (I) and (II) but its intensity is much weaker in compound (III).*


(I)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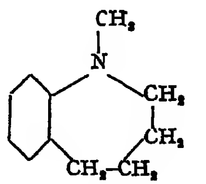
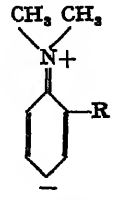

(III)


(IV)

Remington's interpretation was that the contribution of the planar structure (IV) is decreased by the steric hindrance of the group R, and a bulky tertiary butyl group almost excludes this contribution altogether.† Therefore, in view of the steric structure of the triphenylmethyl radical, it seems reasonable to assume that its resonance is almost completely suppressed by the steric hindrance. The weakening of the C—H bond in triphenylmethane can be caused by mutual steric hindrance of the bulky phenyl groups, when forced from the planar configuration of the tervalent carbon into the tetrahedral configuration of the triphenylmethane.

The existence of some tension, not caused by the mutual compression of two triphenylmethyl radicals, may be seen from the observation of Bowden.[23] He found that the radical $(C_6H_5)_3 . C . O—$ is spontaneously rearranged into radical $(C_6H_5)_2 . \underset{|}{C} . O\,C_6H_5$, and this rearrangement will naturally lessen the tension caused by the three phenyl groups previously attached to the one carbon atom.

The Recombination of Triphenylmethyl Radicals.

The great weakening of the C—C bond in hexaphenylethane, we attribute to two steric factors: (1) the repulsion caused by the steric hindrance between two triphenylmethyl radicals, (2) the tension caused by the mutual steric hindrance between the three phenyl groups when tetrahedrally arranged round the central C atom. It is not easy to differentiate between these two effects. For example, the *ortho* groups in derivatives of hexaphenylethane probably influence both effects, decreasing the bond strength of the C—C bond.‡ The increase of the size of the central atom (changing C for Ge, Sn or Pb), influences both effects in the opposite direction, making the corresponding organo-metallic compounds quite stable.[24] The best way for such a differentiation is that chosen by Bent,[20, 25] as described earlier in that paper.

[22] Remington, *J. Amer. Chem. Soc.*, 1945, 67, 1838.
[23] Bowden, *J. Chem. Soc.*, 1939, 26.
[24] Morris, Byerly and Selwood, *J. Amer. Chem. Soc.*, 1942, 64, 1727.
[25] Bent and Cline, *ibid.*, 1936, 58, 1624.

* We should note that the ring in (I) and (II) can be planar, but not in (III).

† The study of the adsorption spectra of the substituted nitro-componds leads to the same conclusion (Brown and Reagen, *J. Amer. Chem. Soc.*, 1947, 69, 1032).

‡ Cp. however, Preckel and Selwood, *J. Amer. Chem. Soc.*, 1941, 63, 3397.

There is, however, clear evidence that the recombination of triphenylmethyl radicals is hindered, as should be expected if there is a steric repulsion between the two radicals. We may recall Ziegler and collaborators [26] who concluded that the recombination of the triphenylmethyl radicals involves an energy of activation of about 8 kcal., necessary for the compression of the phenyl groups, before the C—C bond can be formed. This was shown by finding the energy of activation for the dissociation of hexaphenylethane into radicals to be 19 ± 1 kcal., whereas the heat of dissociation is 11 kcal. only.

That such a compression starts in a distance much bigger than the normal C—C separation is seen from the calculation previously mentioned. It was shown that in two colliding triphenylmethyl radicals the *ortho* H atoms are elevated from the plane passing through central C atom perpendicular to the C—C line by 1·1 A., and therefore the repulsion between the two radicals will effectively start when the two central C atoms are approached to about 4·5 A., which is, of course, much more than the range of chemical forces between the carbon atoms.

It is known that the triphenylmethyl radicals are oxidised very easily to the peroxide, whereas the benzyl radical stabilises itself in an atmosphere of oxygen by dimerisation rather than by oxidation (as was shown by Horrex and Szwarc).[6] This is also evidence of the greater difficulty in the dimerisation of the triphenylmethyl radicals as compared with the benzyl radicals. Further evidence is provided by the study of Magee and Daniels [27] of the photo-bromination of phenyl methanes. The length of the chains in these photobrominations were 50 for toluene, 250 for diphenyl methane and 1000 for triphenylmethane. It is probable that the chains are ended by the dimerisation of the radicals, and thus a shorter chain implies a greater ease of dimerisations.

Conclusion.

We conclude that the most probable value for the resonance energy of the benzyl radical is 24·5 kcal. This value results from the direct measurement of the C—H bond strength in the methyl group of toluene,[1] when compared with the recent value for the C—H bond strength in methane due to Kistiakowsky [28] and Stevenson.[29]

The proposed resonance energy of the benzyl radical leads to the value of 2·09 e.v. or 48 kcal. for the exchange integral, which is only slightly higher than the value of 1·92 e.v. given by Sklar.[12] In addition it seems that this value for the resonance energy of the benzyl radical is in agreement with observations of the C—C bond energy in the polyphenylethanes. It seems also that the weakening of the C—C bond energy of the hexaphenylethane is mainly a steric problem, and so we return to the point fully recognised and emphasised by Ziegler.[30]

The author would like to express his gratitude to Prof. M. Polanyi for his continued interest and encouragement and his many helpful suggestions. His thanks are also due to Manchester University for the I.C.I. Fellowship which enabled him to carry out this work, and to the Anglo-Iranian Oil Company for a grant.

Summary.

Both qualitative and quantitative evidence for the high value of the resonance energy of the benzyl radical has been reported. It is concluded that the most

[26] Ziegler, Orth and Weber, *Annalen.*, 1933, **504**, 131; Ziegler, Seib, Knoevangel and Anders, *ibid.*, 1942, **551**, 161.

[27] Magee and Daniels, *J. Amer. Chem. Soc.*, 1940, **62**, 2825.

[28] Kistiakowsky and van Artsdalen, *J. Chem. Physics*, 1944, **12**, 469.

[29] Stevenson, *ibid.*, 1942, **10**, 291.

[30] Ziegler, *Trans. Faraday Soc.*, 1934, **30**, 10.

probable value for that resonance energy is 24·5 kcal. It is shown that this leads to a higher value of α, the exchange integral, of about 48 kcal. The shortening of the C—C bond in dibenzyl is explained by an increase in the bonding forces, which increases the energy of that bond by 11-13 kcal., and the effect is generalised. The weakening of the C—C bond in hexa-aryl ethanes is explained in terms of two steric repulsions: the repulsion between two radicals and the repulsion among the phenyl groups forced from the planar arrangement into tetrahedral arrangement. The recombination of triphenyl methyl radicals is discussed.

Résumé.

Des mesures directes de la force de la liaison C—H dans le groupe méthyle du toluène, comparée à sa valeur dans le méthane, donnent, pour l'énergie de résonance du radical benzyle, une valeur de 24·5 kcal. Celle-ci conduit à une intégrale d'échange de 48 kcal. et est en accord avec les valeurs de l'énergie de la liaison C—C dans le polyphényl-éthane.

Zusammenfassung.

Der Wert der Resonanzenergie des Benzylradikals, der sich aus der direkten Messung der C—H Bindungsstärke in der Methylgruppe in Toluol im Vergleich zu deren Wert in Methan ergibt, wird als 24·5 kcal. angegeben. Daraus folgt, dass das Austauschintegral den Wert 48 kcal. hat und stimmt auch mit dem Wert der Bindungsenergie in Polyphenyläthan überein.

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SOME REMARKS ON THE CH_2==CH_2 MOLECULE.

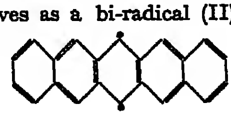
BY M. SZWARC.

Received 13*th August*, 1947.

There is a simple and unambiguous definition of a mono-radical: a neutral molecule, which has one unpaired electron, and which is therefore paramagnetic. The definition of a bi-radical seems to be rather more difficult. A generalisation of the definition of a mono-radical leads to the following criterion: a bi-radical is a neutral molecule endowed with two unpaired electrons (and therefore paramagnetic). A review of the experimental evidence shows, however, that very often the primary bi-radical stabilises itself by a rearrangement of bonds, and as a result a diamagnetic molecule is formed. It seems, however, that the energy levels of the bi-radical and of the corresponding diamagnetic molecule are very close to each other; and it is impossible to draw a sharp distinction between bi-radicals and normal molecules. The following examples will illustrate this.

Pentacene (I), synthesised by Clar,[1] behaves as a bi-radical (II). It was

(I)

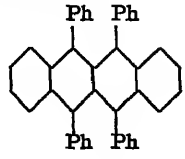


(II)

shown, however, that the molecule is diamagnetic.[3] The case of rubrene (III), prepared by Moureu and Dufraise [2] is similar. The ease with which this compound undergoes oxidation was taken as a strong argument in favour of the bi-

[1] Clar, *Ber.*, 1932, 65, 503.
[2] Moureu and Dufraise, *Bull. Soc. chim.*, 1933, 53, 789.

radical structure (IV), but the investigation of Müller [3] showed that this molecule too is diamagnetic.



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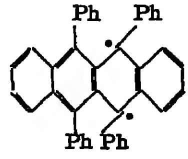
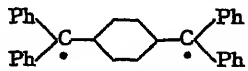


(IV)

It could be expected that the bi-radical character will be much more pronounced in the compounds (V) and (VI). However, the observation [3] that these



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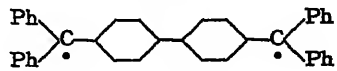
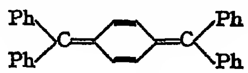
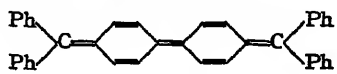


(VI)

compounds are diamagnetic favoured the structures (VII) and (VIII).

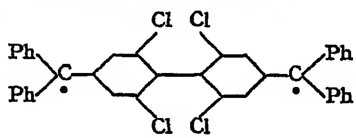


(VII)



(VIII)

If now such a molecule as (VIII) is modified so that it cannot adopt a coplanar arrangement, e.g. by introducing bulky groups in the *ortho* positions, then the resulting compounds are paramagnetic, e.g. (IX).[5]



(IX)

The above-mentioned compounds are rather complicated, and it is therefore of interest that the pyrolysis of *p*-xylene [7] has thrown up evidence concerning the hydrocarbon (X) which has not been previously synthesised.

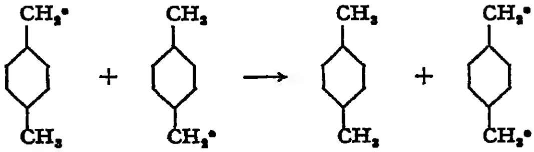
(X)

This hydrocarbon is especially interesting because it is an isomer of cyclo-octatetraene, and in some reactions cyclo-octatetraene behaves as (X). For example, oxidation of cyclo-octatetraene with hypochlorites takes place with the formation of derivatives of *p*-xylene, and oxidation with chromic acid in glacial acetic acid produces terephthalic acid.[6]

The above-mentioned study of the pyrolysis of toluene and the xylenes [7] has shown that the first step in the decomposition of these hydrocarbons is a splitting into benzyl (or xylyl) radicals and hydrogen atoms. It was shown that all the benzyl radicals dimerise giving di-benzyl, whereas the *m*-xylyl radicals gave 3 : 3′-dimethyl-dibenzyl. The pyrolysis of *p*-xylene, however, gave a polymer as the solid product, and a quantitative study proved that the amount of polymer formed corresponds to one half of the *p*-xylyl radicals produced in the original decomposition. It was also found that no products other than *p*-xylene were formed from the second half of the *p*-xylyl radicals. It was thought,

[3] Müller and Müller-Rodloff, *Annalen*, 1935, 517, 134.
[4] Schönberg, *Trans. Faraday Soc.*, 1936, 32, 514.
[5] Müller and Tietz, *Ber.*, 1941, 74, 807.
[6] Reppe, B.I.O.S. Report, No. 137 (1945).
[7] Szwarc, *Nature*, 1947, 160, 403; *J. Chem. Physics*, 1948, 16, 128.

therefore, that the *p*-xylyl radicals disproportionate in the gas phase according to the following equation:



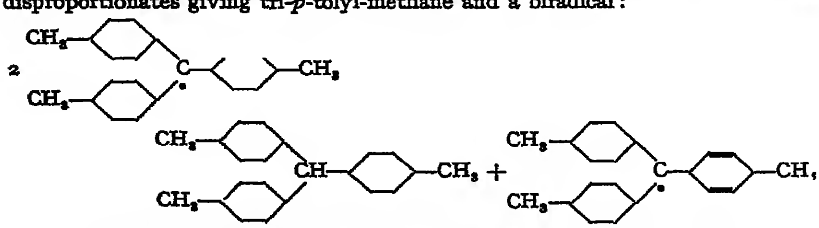
while the bi-radical so formed stabilises itself by passing into the form (X).

In order to prove this assumption iodine vapour was admitted to the trap through which the products of pyrolysis passed and in which the polymer formed. After the experiment the contents of the trap was divided into several portions, and each was extracted with a different solvent, namely, boiling toluene, boiling benzene, boiling chloroform, boiling alcohol and ether respectively. The polymer is insoluble in all these solvents. The extracts were freed from iodine and the solvent evaporated. All the residues thus obtained melted between 160° c. and 170° c. with decomposition and liberation of iodine. A single recrystallisation of the residues from chloroform sufficed to produce nearly white crystals, having the melting point 173°-175° c. The analysis of these crystals gave 71 % iodine.

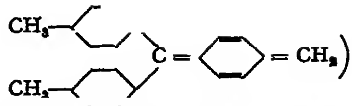
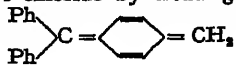
p-Xylylene di-iodide ($CH_2I . C_6H_4 . CH_2I$) has a m.p. 174°-175° c. and an I_2 content of 71·0 %. The m.p. of *p*-xylyl iodide ($CH_3 . C_6H_4 . CH_2I$) is 46°-47° c. The results described above leave no doubt therefore that the only product formed in the experiment, apart from the polymer, is *p*-xylylene di-iodide, with minute quantities of impurities only; which finally proves the existence of the hydrocarbon (X) in the gas phase.

The hydrocarbon (X) seems to be very stable in the gas phase, if its presseur is low enough. It will travel a couple of metres in the glass tube, and passes through glass capillaries without leaving any deposit. It was found that the formation of the polymer corresponds closely to the condensation of a vapour. If the partial pressure of the monomer (X) is increased (by increasing the total pressure of the pyrolysed *p*-xylene, or by increasing the % decomposition) the polymer starts to form in a tube heated to 50° c., while if its partial pressure is lower, the polymerisation does not start until it reaches a tube cooled to 0° c., and at still lower concentration of the monomer in the streaming gas the tube must be cooled to − 80° c. to cause the formation of the polymer. It is very significant that if the vapour passes through two traps, the first cooled to 0° c., and the second to − 80° c., and the concentration of the monomer (X) in the vapour is high enough to cause the formation of the polymer at 0° c., two portions of polymer are obtained: one formed in the trap at 0° c., and the second in the trap at − 80° c., but the tube connecting the two traps, which is at room temperature, remains clear. This phenomenon can be explained in the following way: the partial pressure of the monomer in the gas stream entering the first trap exceeds its saturation pressure corresponding to 0° c., and therefore the monomer condenses and starts immediately to polymerise in the condensed phase. The partial pressure of the monomer retained in the gas stream on leaving the first trap is that of the saturated vapour at 0° c., and therefore no condensation (and no polymerisation) occurs in the tube leading to the second trap, which is at room temperature, while the condensation once more starts in the second trap, cooled to − 80° c., causing the formation of an additional portion of the polymer here.

Two cases of similar polymerisation are reported in the literature. One is the polymerisation of the products of dissociation of hexa-*p*-tolyl-ethane. Marvel and his co-workers [8] found, tht the resulting tri-*p*-tolyl-methyl radical disproportionates giving tri-*p*-tolyl-methane and a biradical:



[8] Marvel, Rieger and Muller, *J. Amer. Chem. Soc.*, 1939, 61, 2769.

This biradical (or its quinonoid form  poly-merises giving a glassy residue. The second example is the polymerisation of a similar quinonoid compound investigated by Schlenk and Mayer.[9] They succeeded in abstracting HCl from di-phenyl-*p*-tolyl-methyl chloride by treating it with pyridine, and obtained the quinonoid compound  which was found to polymerise to a resin.

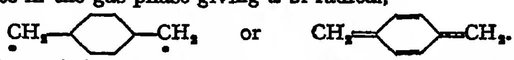
To sum up, we conclude that the  hydrocarbon seems to be stable in the gas phase and its condensation is governed by the normal phase rule. From our observations we would roughly estimate that its saturation pressure at 50° c. is 0·3 mm. Hg. In the condensed phase the $CH_2 : C_6H_4 : CH_2$ is unstable and polymerises giving a transparent, or white, film at 0° c. and a white fibrous solid at − 80° c. The polymer is insoluble in boiling organic solvents such as toluene, benzene, ether, chloroform and alcohol. It resists the action of conc. H_2SO_4 at 100° c. It is not volatile and does not soften up to 175° c.

The  molecule is an example of a compound which is stable in the gas phase, but labile in the condensed phase; and that is the reason why it has not been synthesised by the normal methods of organic synthesis.

The author would like to express his gratitude to Prof. M. Polanyi for his continued interest and encouragement. His thanks are also due to Manchester University for the I.C.I. Fellowship which enabled him to carry out this work, and to Anglo-Iranian Oil Co., for a grant.

Summary.

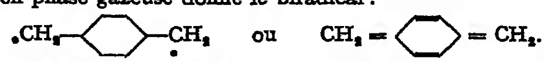
It is shown that the *p*-xylyl radical, formed in the pyrolysis of *p*-xylene, disproportionates in the gas phase giving a bi-radical,



This bi-radical is stable in the gas phase, and behaves as an ordinary condensable vapour, but it is labile in the condensed phase, undergoing immediate polymerisation. The polymer formed is not volatile and is insoluble in boiling organic solvents.

Résumé.

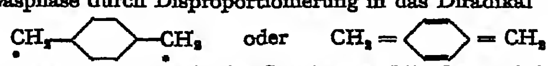
On montre que le radical *p*-xylyle, formé dans la pyrolyse du *p*-xylène, par dismutation en phase gazeuse donne le biradical:



Le biradical est stable en phase gazeuse et labile en phase condensée, se polymérisant immédiatement. Le polymère ainsi formé n'est pas volatile et est insoluble dans les solvants organiques bouillants.

Zusammenfassung.

Es wird gezeigt, dass das aus *p*-Xylol pyrolytisch gebildete *p*-Xylylradikal sich in der Gasphase durch Disproportionierung in das Diradikal



umwandelt. Das Diradikal ist in der Gasphase stabil, aber labil in der flüssigen Phase, wo es sofort polymerisiert. Das so erhaltene Polymerprodukt ist nicht flüchtig und in sied enden organischen Lösungsmitteln unlöslich.

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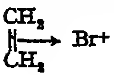
[9] Schlenk and Meyer, *Ber.*, 1919, 52, 9.

CALCULATED HEATS OF FORMATION OF SOME π-COMPLEXES.

By M. J. S. Dewar.

Received 25th July, 1947.

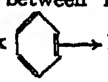
In three recent papers [1] a number of organic reactions were interpreted in terms of a new type of bond; a dative bond in which the donor molecule carries π-electrons and not unshared p-electrons. Thus the intermediate cation in the addition of Br_2 to C_2H_4 was formulated as (I), implying that the bromine is attached by a bond formed by the ethylenic π-electrons, the bond-orbital covering all three nuclei. This idea is inherently reasonable since the main criteria for bond-formation are that the two relevant orbitals should overlap efficiently and that they should between them contain two electrons. The second criterion is automatically satisfied in the cases under consideration, while the close similarity between p- and π-orbitals suggests that the latter should overlap efficiently with atomic or π-orbitals of other molecules.



(I)

In the earlier papers it was shown that the chemical evidence justified belief in this "molecular bond" as we may conveniently term it; here the new bond will be investigated theoretically, and we shall see that the calculations, although by necessity very approximate, further justify belief in its existence.

Method.

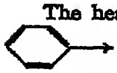
In this preliminary treatment Hückel's original method has been used for simplicity. The energies of formation of a number of π-complexes from their components have been calculated with the assumption that all exchange integrals are equal to β, the C—C exchange integral, and with the neglect of exchange integrals between non-adjacent atoms. Thus the secular equation for the π-complex  X^+ is taken to be

$$\begin{vmatrix} w & \beta & \beta & 0 & 0 & 0 & 0 \\ \beta & w & \beta & 0 & 0 & 0 & \beta \\ \beta & \beta & w & \beta & 0 & 0 & 0 \\ 0 & 0 & \beta & w & \beta & 0 & 0 \\ 0 & 0 & 0 & \beta & w & \beta & 0 \\ 0 & 0 & 0 & 0 & \beta & w & \beta \\ 0 & \beta & 0 & 0 & 0 & \beta & w \end{vmatrix} = 0$$

Differences in electron affinity have in general been neglected. In most cases the secular equations can be factorised.

The assumption that the new exchange integrals have the value β is of course arbitrary, but it is unlikely to be much in error since the length-wise overlapping of the p-orbitals involved should be at least as efficient as the lateral overlapping in a normal double bond. Coulson [2] has raised a further objection, that the longitudinal sharing of π-electrons should alter the hybridisation of the atoms forming the donor component of the molecular bond. It is difficult to estimate the magnitude of this effect; but since it must lead to an increase in stability of the molecule as a whole, it can imply only that the heats of formation here calculated are too low. This will certainly not affect our conclusions.

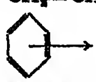
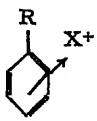
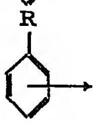
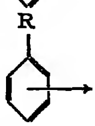
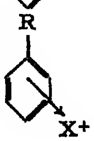
Results.

The heats of formation thus calculated are given in Table I. The symbol  X^+ implies a configuration of the π-complex in which X is opposite

[1] Dewar, *Nature*, 1945, 176, 784; *J. Chem. Soc.*, 1946, 406, 707.
[2] Private communication.

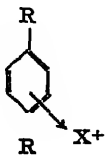
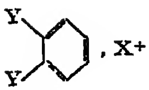
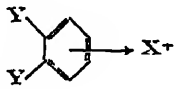
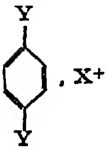
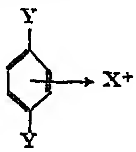
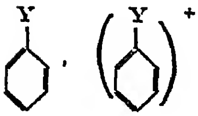
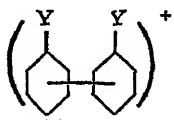
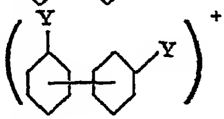
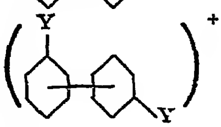
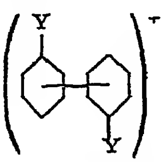
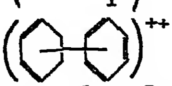
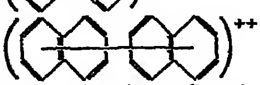
an annular carbon so that only one C—X exchange integral is included, while the symbol  X+ implies a configuration where X+ is equidistant from two ring carbons. the exchange integrals to both being included. In Table II are given electron densities and bond-orders for the π-complexes from unsymmetrical ethylenes. In the substituted benzenes Y represents a group with unshared *p*-electrons and serves as a model for an anionoid-electromeric *o*—*p*-directing substituent; Z represents a group with a vacant orbital and serves as a simple model of a cationoid-electromeric *m*-directing substituent.

TABLE I.

Components.		π-complex.		Heat of Formation $\times \beta^{-1}$.	
$CH_2{=}CH_2$, X^+		$CH_2{=}CH_2 \rightarrow X^+$	(II)	2·000	
$CH_2^*{=}CH_2$, X^+	(*a*)	$CH_2^*{=}CH_2 \rightarrow X^+$	(III*a*)	2·228	
$CH_2^*{=}CH_2$, X^+	(*b*)	$CH_2^*{=}CH_2 \rightarrow X^+$	(III*b*)	1·592	
$CH_2{=}CH{-}CH{=}CH_2$, X^+		$CH_2{=}CH{-}CH{=}CH_2 \rightarrow X^+$	(IV*a*)	1·956	
		$CH_2{=}CH{-}CH{=}CH_2 \rightarrow X^+$	(IV*b*)	1·370	
 , X+		 X+	(V*a*)	1·656	
		 X+	(V*b*)	0·720	
				R = Y	R = Z
 , X+			(VI*a*)	1·707	1·387
		 X+	(VI*b*)	1·232	0·642
		 X+	(VI*c*)	1·820	1·408
			(VI*d*)	0·710	0·120

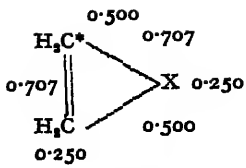
(*a*) C* has an electron affinity $-\beta$ relative to carbon.
(*b*) C* has an electron affinity $+\beta$ relative to carbon.

TABLE I (*cont.*).

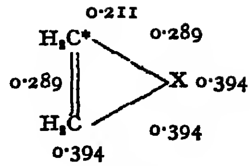
Components.	π-complex.		Heat of Formation $\times \beta^{-1}$.	
		(VI*e*)	1·744	1·436
		(VI*f*)	0·724	0·134
		(VII)		2·098
		(VIII)		1·876
		(IX)		2·000
		(X)		1·548
		(XI)		1·428
		(XII)		0·882
		(XIII)		2·000
		(XIV)		2·764
		(XV)		2·970

(*a*) C* has an electron affinity $-\beta$ relative to carbon.
(*b*) C* has an electron affinity $+\beta$ relative to carbon.

TABLE II.



(III*a*)



(III*b*)

Conclusions.

(1) The relatively large heat of formation ($\sim$ 40 kcal.[3]) of the simple π-complexes (II) and (III) certainly suggests that they may be intermediates in reactions. The further addition of an anion to such a π-complex should take place at the more positive carbon and the one more weakly linked to X. The electron-densities and bond-orders in (III*a*) and (III*b*) suggest that an anionoid substituent, which will lower the electron-affinity of the adjacent carbon, should favour addition of the anion to that carbon in accordance with Markownikov's rule while a cationoid substituent should have the opposite effect. Moreover the π-complex stability is increased by anionoid, decreased by cationoid substitution of the double bond, in accordance with experimental evidence that anionoid substituents increase, cationoid decrease, the rate of addition to olefines.

(2) The π-complex from butadiene has a heat of formation slightly less than that from ethylene; but the simple allyl cation

$$(XCH_2\text{—}CH\cdots CH\overline{\ \ }CH_2)^+,$$

postulated as an intermediate in the classical mechanism, has a relatively large resonance energy (15 kcal. in the present approximation). Very probably cationoid addition to butadiene takes place by the classical mechanism, and it is interesting that addition of anions (which must occur by the classical mechanism) is observed in butadiene but not in simple olefines.

(3) The relatively large heats of formation of π-complexes from active cations and benzene derivatives (IV, V) support the π-complex mechanism [1] for cationoid substitution. Also anionoid substituents again increase, cationoid decrease, the stability of the π-complexes, in agreement with experimental evidence that the former increase, the latter decrease, the rate of substitution. The present theory does not predict the orientation of the products, since this depends on the relative rates of secondary reactions of the π-complex. These latter reactions presumably proceed through classical transition states of the type considered theoretically by Wheland.[4]

(4) The high heats of formation of (VI) and (VII) suggest that di-substituted compounds such as veratrole or hydroquinone dimethyl ether should substitute more easily than the monosubstituted analogue (e.g. anisole). This certainly seems to be so,[1] although the classical electronic theory would require them to be less reactive.

(5) The stability of the model benzidine intermediates falls in the series (VIII) $\gg$ (IX) $>$ (X) $\gg$ (XI). Since (VIII) and (IX) should be preferentially destabilised by coulomb repulsion of the nitrogen atoms, which will carry most of the positive charge, it is reasonable that the actual order of stability should be (VIII) $>$ (X) $>$ (IX) $>$ (XI), as experiment requires.[1] Incidentally the great ease of rearrangement of hydrazobenzene is easily intelligible since the calculated heats of formation of the π-complexes are comparable with the N—N bond-energy.

[3] The exchange integral has the value 18 kcal. in this approximation.
[4] *J. Amer. Chem. Soc.*, 1941, 63, 909.

(6) Weiss [5] has reported that oxidation of solutions of aromatic hydrocarbons in concentrated sulphuric acid gives coloured products which, he claims, contain ion-radicals $(C_nH_m)^+$. The calculations (XII, XIII, XIV) suggest that the products may be π-complex dimers $(C_nH_m)_2^{++}$ of those radicals. The heat of dimerisation will be less by the coulomb energy of dimerisation, but in a solvent of very high dielectric constant (e.g. H_2SO_4) the latter may be quite small.

Summary.

The heats of formation of a number of π-complexes [1] have been calculated by Hückel's molecular orbital method. The heats of formation are large and support the conclusions previously reached [1] on qualitative grounds. A π-complex structure is suggested for the products obtained by oxidation of aromatic hydrocarbons in sulphuric acid.

Résumé.

On a calculé par la méthode des orbites moléculaires de Hückel, les chaleurs de formation de certains complexes-π. Elles sont importantes et viennent appuyer les conclusions précédemment atteintes à partir de bases qualitatives. On suggère une structure de complexe-π pour les produits de l'oxydation d'hydrocarbures aromatiques dans l'acide sulfurique.

Zusammenfassung.

Die Bildungswärmen von einer Anzahl von π-Komplexen wurde nach Hückel's Methode der molekularen Elektronenzustände berechnet. Die Bildungswärmen sind gross und bestärken die früher auf qualitative Argumente gestützten Folgerungen. Es wird eine π-Komplexstruktur für die Produkte der Oxydation von aromatischen Kohlenwasserstoffen durch Schwefelsäure vorgeschlagen.

Courtaulds, Limited,
The Islet,
Maidenhead Court,
Maidenhead.

[5] *Nature*, 1941, 147, 512.

DIFFICULTIES IN THE APPLICATION OF MOLECULAR ORBITAL THEORY TO MESOMERIC IONS.

By C. A. Coulson and M. J. S. Dewar.

Received 5th February, 1948.

The interest roused by the earlier paper in this Discussion by one of us (M.J.S.D., p. 50) prompts us to make a little clearer the nature of the approximations involved in the treatment that was given there. For it is important to know the kind of accuracy and reliability that we may reasonably expect to find in this type of calculation. We may divide these approximations into two groups, the first of which relates to all molecular-orbital work and the second more specifically to the calculations at present under review.

In the first group we can place :

(i) The representation of a molecular orbital (MO) as a linear sum of atomic orbitals (LCAO approximation).

(ii) The neglect of all "overlap" integrals $\int \phi_r \phi_s dv$, where r and s are any pair of distinct atoms. For neighbouring carbon atoms, this integral is known to be about 1/4.

(iii) The use of one common value for all the resonance integrals $\beta_{rs} = \int \phi_r \mathscr{H} \phi_s dv$, independent of the bond lengths. In accurate work by Lennard-Jones [1] for butadiene, where the disparity in bond lengths is admittedly greater than in the molecules dealt with by Dewar, the values of the resonance integrals for the short and long bonds are in the ratio 5 : 4.

(iv) The neglect of all electron exchange other than that which is associated with an average field for one electron, provided by all the other electrons and the nuclei.

(v) An essential inaccuracy in all cases where the π-electron distribution is not uniform, leading [2] to the conclusion that in its present form the method is not genuinely self-consistent.

(vi) An inadequate allowance for the repulsive terms in the total energy, so that [3] molecules appear to show a spurious additional affinity for other atoms.

(vii) The assumption that π-electron energies can be calculated without considering any perturbation of the other (i.e. σ) electrons in the molecule.

(viii) The assumption that the contribution to the total energy of the molecule which arises from nuclear Coulomb repulsions is adequately expressed by a single term E_0 (in the usual notation). For by the MO method one essentially calculates the energy levels of a single electron moving in the field due to a fixed framework of nuclei and averaged positions of the other electrons. At first sight, therefore, it appears completely to neglect the Coulomb repulsions. In fact they are chiefly included (rather clandestinely) in the E_0 term by assuming that the total energy of the molecule is

$$E_\sigma + mE_0 + k\beta,$$

where E_σ is the contribution from the σ-bonds, m is the number of π-electrons and k is a constant for each molecule found by solution of the appropriate secular equations. It is usual to neglect variations of E_σ, as these bonds are localised, and to treat E_0 as a constant independent of the number of unsaturated nuclei. In a formal manner E_0 is defined in terms of the Hamiltonian $\mathscr{H}$ for a single electron by

$$E_0 = \int \phi_r \mathscr{H} \phi_r dv.$$

Now according to this argument, if it were possible to localise the π-electrons ($\beta = 0$) the energy would be $E_\sigma + mE_0$. It follows that $k\beta$ is the delocalisation energy of the mobile electrons. Therefore the internuclear Coulomb terms (if they are included at all) must be included partly in E_σ and partly in E_0; it is only in a secondary way that they are included in β. This may be verified in more detail later (see eqn. (14) and (15)) where it is also shown that the interelectronic Coulomb terms appear chiefly in β. We now see that the fundamental approximation here involved is that of supposing that these two types of Coulomb repulsion depend in a linear way solely upon the numbers of σ-bonds and π-electrons, and their delocalisation energy. No account is taken either of the stereochemistry of the molecule or of its internuclear distances.

Concerning these difficulties, it is probable that (i) is allowed for fairly adequately by a suitable choice of β. It is also probable [4] that (ii) is not serious for calculations of the ground states of hydrocarbon molecules, though it is more serious for excited states, and, as Mulliken,

[1] *Proc. Roy. Soc. A*, 1937, **158**, 280.
[2] Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193.
[3] Van Vleck and Sherman, *Rev. Mod. Physics*, 1935, **7**, 167.
[4] Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 2025.

Rieke and Brown [5] have shown explicitly, it is a more serious objection still when atoms of different electronegative character are used. Similarly, for hydrocarbon molecules, variations of β from one bond to another, referred to in (iii) and (viii) do not affect the energy significantly in the ground state. (iv) is quite unavoidable in all simple MO work, and completely spoils all *a priori* calculations of excitation energies. (v) is also unavoidable, and no-one can say how serious is the limitation of accuracy which it introduces. One can say, however, that any attempt to calculate the u.-v. absorption of hetero-molecules by this type of method seems to be completely hopeless, and doomed to failure. Difficulty (vi) is quite serious, as one can see as follows.

The binding energy for H_2 calculated according to the simple MO treatment is 2β. The binding energy for linear H_3 is $2{\cdot}828\beta$, suggesting that H_3 should be more stable than H_2 by $0{\cdot}828\beta$. This is quite wrong, being far too large. Further, equilateral H_3 has a binding energy no less than 3β. Unfortunately it is known [6] that linear H_3 is actually more stable than equilateral H_3. Quite evidently by this method one calculates largest binding energy when as many nuclei as possible are within bonding distance of each other. This is because (see later) the repulsive terms are not adequately included.

The affinity for ions is even more pronounced. Thus the energy for H_2 is 2β, but that for linear H_3^+ is $2{\cdot}828\beta$, and for equilateral H_3^+ is 4β. It is true [7] that the triatomic hydrogen ion is the more stable in an equilateral shape than a linear one, but the value 4β for H_3^+ is vastly too big. It is even worse for the square molecule H_4^{++}, which is calculated to have the same binding energy as H_3^+, that is, twice the binding energy of H_2.

Difficulty (vii) has never been discussed in a quantitative manner, and it is not at present possible to estimate its importance. But in all cases where ionic or polar effects are taking place, we must expect some kind of polarisation of the σ-electrons. Further, since the internal fields in molecules which result from an uneven distribution of charge are extremely large (some millions of volts per cm.) it may easily happen that an appreciable omission is being made in this respect.

Difficulty (viii) is almost certainly significant. For the assumption of a constant E_0 implies that all carbon atoms in a conjugated system are equivalent electronegatively. Thus for a chain molecule it neglects "end-effects" which are now known from accurate calorimetric measurement not to be negligible; and for a condensed molecule like naphthalene it treats one of the inner atoms 9 and 10 which are surrounded by three other carbons, as being under the same Coulomb forces as the outer atoms 1-8, only two of whose neighbours are carbon and the other hydrogen.

In view of the comments above, we are forced to conclude that the simple MO method as at present used, is semi-empirical in the sense that no *a priori* estimate can be made of the probable errors involved. Moreover it is known to fail badly in at least one case (light absorption) where a quantitative test is possible. Any extension of the calculations to new types of compound must therefore be experimentally checked before any confidence can be placed in their quantitative significance.

The second group of assumptions is more specific to the use of MO theory for ions. This concerns both simple ions (cp. Wheland [8]) and, *a fortiori*, π-complexes. We may list:

(ix) The use of a single value of β both for the neutral molecule and for the cation, or anion. It is true that the binding energy of H_2^+ is about

[5] *J. Amer. Chem. Soc.*, 1941, 63, 41.
[6] Eyring, Rosen and Hirschfelder, *J. Chem. Physics*, 1936, 4, 121, 131.
[7] Coulson, *Proc. Camb. Phil. Soc.*, 1935, 31, 244.
[8] *J. Amer. Chem. Soc.*, 1942, 64, 900.

half that of H_2, suggesting that the same value of β may be used for both. But the use that we are now considering arises in the addition of another atom to an already existing molecule. When we pass from H to H_2^+ by the addition of a proton, the screening is distinctly altered, so that (in atomic units) an atomic wave function e^{-r} becomes a molecular wave function $e^{-cr_a} + e^{-cr_b}$, where c is a parameter whose numerical value is about 1·2. For that reason, if for no other, we may expect a new β to apply, for example, to H_2^+ as compared with H_2.

(x) The use of the same Coulomb term E_0 for the carbon atoms both in the neutral and ionic molecules. If we compare $\begin{matrix} H_2C \\ \| \\ H_2C \end{matrix}$ and $\begin{matrix} H_2C \\ \|\!\rightarrow X^+, \\ H_2C \end{matrix}$ we shall expect to find less electronic charge on each of the carbon atoms in the second case. Therefore, as Walsh [9] has shown for the oxygen atom in different carbonyl bonds, we shall anticipate changes in the electron affinity (or electronegativity, or Coulomb) terms $\int \phi_r \mathscr{H} \phi_r \, dv$. These changes may easily amount to 5 or 10 kcal.

(xi) Assumption (vii) above, which is used when discussing neutral molecules, is even harder to justify for ions, as a very simple argument will show. The calculated π-electron energies in the allyl cation, radical and anion are respectively $2E_0 + 2\beta$, $3E_0 + 2\beta$ and $4E_0 + 2\beta$ (E_0 and β are negative). This means, according to what we said in (viii), that the allowance for repulsion will be, at most, doubled over this series. Now in the cation, radical and anion there are 2, 3 and 4 electrons, involving 1, 3 and 6 electron-interaction terms respectively. So, even if the inter-nuclear repulsions remain substantially the same on account of roughly similar bond lengths, the inter-electronic repulsions increase rapidly and non-linearly. Our rough calculations suggest that this effect may be large. It is true that it will be counterbalanced by the changes in β (see (ix)) which will presumably be opposite in sign, and possibly also by changes in the overlap integrals. But we certainly cannot say that all these changes will compensate one another as they must do if the MO method is to work adequately for ions. The only experimental evidence comes from the relative basic strengths of mesomeric and non-mesomeric anions, and it does suggest that the MO method gives reasonable results. Thus the acid strengths of toluene and cyclopentadiene are of the order of magnitude expected from the calculated resonance energies of the benzyl and cyclopentadienyl anions. But this kind of evidence is totally inadequate at present.

The use of MO theory by Dewar involves one further assumption and one over-simplification.

(xii) In any exact calculations it would certainly be necessary to take into account differences in the Coulomb terms for the cationic nucleus X and carbon. It is known that many of the characteristic effects in conjugated systems arise from the difference in electronegative character of one or more of the atoms. Recent theories of chemical reactivity [10] make explicit use of this fact. In the form in which Dewar's calculations have been made, it is assumed that the C and X atoms have the same electronegativity. But C—Cl and C—Br bonds do not have zero dipole moment, and some unpublished work of Longuet-Higgins on C_2Cl_4 shows that no satisfactory interpretation of its bonds which treats the Cl atoms as if they were carbon is possible. Since the atoms X are more electro-negative than carbon, this approximation will make the binding energies calculated by Dewar too low.

(xiii) The assumption that "end-wise" overlap of an ethylene bond with the cation is such that the interactions between the σ and π-electrons is the same as before, is hard to substantiate. Indeed, as was stated in

[9] *Trans. Faraday Soc.*, 1947, 43, 158.
[10] Coulson and Longuet-Higgins, *Rev. Sci.*, 1947, 85, 929.

Dewar's paper, the distinction between σ and π-electrons is removed when end-wise overlap takes place, so that we cannot now deal solely with the π-electrons. The situation is best described [11] by saying that a new (partly tetrahedral) hybridisation takes place. An alternative description is to say that there is now resonance between the former σ and π-electrons. But on account of the new repulsive interaction terms that come into the complete Hamiltonian, it would need a very careful analysis to be sure that this σ-π interaction did not give rise to an adverse energy contribution. It will almost certainly be a repulsive energy term.

One further point should be mentioned, since it has aroused some comment. In an ion the various atoms carry net partial charges. The Coulomb energy which results from these net charges (assumed to be concentrated at the nuclei) is apparently not included in the MO calculation. Thus, if the electronic charge in $\begin{array}{l}CH_2\\ \| \rightarrow X^+\\ CH_2\end{array}$ is uniformly shared, the corresponding repulsion between the three net positive charges each equal to $e/3$, is $\frac{3}{r}\left(\frac{e}{3}\right)^2$, or about 87 kcal., which is much greater than the calculated delocalisation energy (36 kcal.). However, this argument must not be used too indiscriminatively. For the repulsions thus described are only one part of the much larger total internuclear and interelectronic repulsions. It is instructive to discuss the matter in terms of the $\left(\begin{array}{l}CH_2\\ \| \rightarrow X\\ CH_2\end{array}\right)^+$ ion, in order to see to what extent a proper choice of E_0 and β is able to allow compensation for the increased Coulomb energies. For this purpose the following very rough calculations may be made.

Let us suppose that the total mobile electron cloud may be treated as if it were located, in proper proportions, exactly at the different nuclei. Then in ethylene there is a total of exactly one π-electron on each nucleus, and the nuclear and electronic repulsions are each equal to e^2/r_1. But in $\left(\begin{array}{l}H_2C\\ \quad \| \rightarrow X\\ H_2C\end{array}\right)^+$, taking the calculations of Dewar in which the atom X is given the same values of the fundamental parameters E_0 and β as a carbon atom, there is a total of $2e/3$ electronic charge on each nucleus. The resulting internuclear and interelectronic repulsions are shown in the Table below, together with the calculated π-energies. In this Table, r_1 is the C—C distance, assumed to be the same as in ethylene, and r_2 is the C—X distance. (If r_2 differs considerably from r_1, then the mobile charge will not be quite uniformly distributed; but we are going to neglect this possible refinement in the calculations.) Now we have given reasons earlier in (viii) for believing that internuclear repulsions are chiefly expressed in the E_0 term, and inter-electronic repulsions chiefly in the β

	Inter-electronic Repulsion	Internuclear Repulsion	Total π-Energy
ethylene	e^2/r_1	e^2/r_1	$2E_0 + 2\beta$
$\left(\begin{array}{l}H_2C\\ \quad \| \rightarrow X\\ H_2C\end{array}\right)^+$	$\frac{4e^2}{9}\left(\frac{1}{r_1}+\frac{2}{r_2}\right)$	$e^2\left(\frac{1}{r_1}+\frac{2}{r_2}\right)$	$2E_0 + 4\beta$

term. It is at once obvious that in order to get consistency in the above Table, the value of E_0 for the ion must be greater than the value of E_0 for ethylene by an amount e^2/r_2. But the value of β for the ion must be less than the value of β for the molecule. Thus, if we use the same values of E_0 and β for both systems, we underestimate the internuclear repulsions

[11] Coulson and Moffitt, *J. Chem. Physics*, 1947, 15, 155, and later work to appear.

and we overestimate the inter-electronic repulsions. We cannot readily conclude what the final result of these mutually compensating effects will be.

It would be unfair to rule out the MO method simply on the basis of an argument such as that just outlined. But these considerations do show that no precise estimate can be made of possible errors. Moreover, when several modes of attachment of the cation are possible (e.g. with benzene, X^+ may be attached to one side, or one corner, of the hexagon, or symmetrically to its centre) we cannot say *a priori* that the MO method will correctly predict their relative energies. That is, the stereochemistry of the resulting π-complex cannot be reliably predicted.

Some of the points raised above can be seen in the following quite elementary discussion of the simplest form of MO theory applied to the ground states of H_2^+, H_2, H_2^- and H_3^+ (linear and equilateral). We have chosen these systems because we thereby dispense with the need to distinguish between σ and π-electrons: and we are able more simply to investigate the addition of a cation (here a proton) to a neutral molecule, and to see how the various energy terms depend upon whether the addition takes place to one of the atoms of the molecule (forming linear H_3^+), or to one of the bonds (forming equilateral H_3^+). The fact that the electrons we are dealing with are all σ-electrons is, of course, quite irrelevant. The formal treatment is exactly the same as if they were π-electrons, with a parallel direction for their orbitals. In the case of H_3, this direction would need to be perpendicular to the plane of the nuclei.

Let us call the nuclei *a, b, c* (in order) and the electrons 1, 2 and 3. Then in atomic units the Hamiltonian for H_2^+ is $\mathscr{H}$, where

$$(H_2^+ \text{ ion})\ \mathscr{H} = -\frac{1}{2}\Delta^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{r_{ab}}. \quad . \quad . \quad (1)$$

The complete Hamiltonian for H_2 is

$$-\frac{1}{2}(\Delta_1^2 + \Delta_2^2) - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{r_{ab}}, \quad . \quad (2)$$

but for the purposes of MO theory we have to average the $1/r_{12}$ term and share the $1/r_{ab}$ term between the two electrons. This means that we are to write (2) in the form

$$\mathscr{H} \simeq \mathscr{H}(1) + \mathscr{H}(2) \quad . \quad . \quad . \quad . \quad (3)$$

where

$$(H_2 \text{ molecule})\ \ \mathscr{H}(1) = -\frac{1}{2}\Delta_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} + \frac{1}{2}\left(\frac{1}{r_{12}}\right)_{\text{av. over } 2} + \frac{1}{2}\frac{1}{r_{ab}}. \quad (4)$$

In this notation $\left(\frac{1}{r_{12}}\right)_{\text{av. over } 2}$ implies that we are to calculate the average value of $1/r_{12}$ for all positions of electron 2, giving us, as is required in any MO representation, a Hamiltonian operator $\mathscr{H}(1)$ for electron 1, which is solely a function of the co-ordinates of this electron. Assuming that the normalised MO wave function for H_2 is $\Phi = \psi(1)\psi(2)$, then

$$\left(\frac{1}{r_{12}}\right)_{\text{av. over } 2} = \int \frac{1}{r_{12}}[\psi(2)]^2 dv_2. \quad . \quad . \quad . \quad . \quad (5)$$

This means that in the simplest MO theory the original term $1/r_{12}$ in (2) is divided equally into two purely Coulomb terms (5), one of which acts on electron 1, and the other electron 2.

For the three-electron molecule H_2^- we have, in this approximation

$$\mathscr{H} \simeq \mathscr{H}(1) + \mathscr{H}(2) + \mathscr{H}(3) \quad . \quad . \quad . \quad (6)$$

where

$$(\text{H}_2^- \text{ ion})\ \mathscr{H}(1) = -\frac{1}{2}\Delta_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} + \frac{1}{2}\left(\frac{1}{r_{12}}\right)_{\text{av. over 2}} + \frac{1}{2}\left(\frac{1}{r_{13}}\right)_{\text{av. over 3}} + \frac{1}{3}\cdot\frac{1}{r_{ab}}. \quad (7)$$

For the triatomic molecule H_3^+ we have similarly

$$\mathscr{H} \simeq \mathscr{H}(1) + \mathscr{H}(2) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$(H_3^+ \text{ ion})\quad \mathscr{H}(1) = -\frac{1}{2}\Delta_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{c1}} + \frac{1}{2}\left(\frac{1}{r_{12}}\right)_{\text{av. over 2}}$$
$$+ \frac{1}{2}\left(\frac{1}{r_{ab}} + \frac{1}{r_{bc}} + \frac{1}{r_{ca}}\right). \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This formula holds both for the linear and the equilateral H_3^+.

In each of the above cases the allowed molecular orbitals ψ are solutions of the one-electron wave equation

$$\mathscr{H}(1)\psi(1) = \mathscr{E}\psi(1). \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In each case, also, we suppose that ψ is a linear combination of normalised atomic orbitals, ϕ_a, ϕ_b and ϕ_c, so that for the two-nuclear molecules H_2^+, H_2 and H_2^- we write (omitting normalisation factors for convenience)

$$\psi_{\pm} = \phi_a \pm \phi_b. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

For the three-nuclear molecule H_3^+ we write

$$\psi = \phi_a + \phi_c + \lambda\phi_b, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where λ is a constant determined from the secular equations. For the equilateral H_3^+, $\lambda = 1$.

In all these calculations we are concerned primarily with what may be called the Coulomb terms E_0 and the resonance integrals β. These are defined by

$$E_0 = \int\phi_a(1)\mathscr{H}(1)\phi_a(1)dv_1,$$
$$\beta = \int\phi_a(1)\mathscr{H}(1)\phi_b(1)dv_1\,. \quad . \quad . \quad . \quad . \quad (13)$$

It follows from (1), (4), (7) and (9) that if we may suppose ϕ_a, ϕ_b and ϕ_c to be the same in all four molecules, and if the overlap integrals such as $\int\phi_a\phi_b dv$ are all taken to be zero, then

$$\beta(H_2) = \beta(H_2^+) + \frac{1}{2}\left\langle\frac{1}{r_{12}}\right\rangle_{ab}$$
$$\beta(H_2^-) = \beta(H_2^+) + \frac{1}{2}\left\langle\frac{1}{r_{12}}\right\rangle_{ab} + \frac{1}{2}\left\langle\frac{1}{r_{13}}\right\rangle_{ab}$$
$$\beta(H_3^+) = \beta(H_2^+) + \frac{1}{2}\left\langle\frac{1}{r_{12}}\right\rangle_{ab} - \left\langle\frac{1}{r_{c1}}\right\rangle_{ab} \quad . \quad . \quad . \quad . \quad (14)$$
$$E_0(H_2) = E_0(H_2^+) - \frac{1}{2}\frac{1}{r_{ab}} + \frac{1}{2}\left\langle\frac{1}{r_{12}}\right\rangle_{aa}$$
$$E_0(H_2^-) = E_0(H_2^+) - \frac{2}{3}\frac{1}{r_{ab}} + \frac{1}{2}\left\langle\frac{1}{r_{12}}\right\rangle_{aa} + \frac{1}{2}\left\langle\frac{1}{r_{13}}\right\rangle_{aa}$$
$$E_0(H_3^+) = E_0(H_2^+) - \left\langle\frac{1}{r_{c1}}\right\rangle_{aa} + \frac{1}{2}\frac{1}{r_{ac}} + \frac{1}{2}\left\langle\frac{1}{r_{12}}\right\rangle_{aa} \quad . \quad (15)$$

In (14) and (15) we have used the notation:

$$\left\langle\frac{1}{r_{12}}\right\rangle_{ab} = \int \phi_a(1)\left(\frac{1}{r_{12}}\right)_{\text{av. over } 2} \phi_b(1)\mathrm{d}v_1 \qquad . \quad . \quad . \quad (16)$$

$$\left\langle\frac{1}{r_{12}}\right\rangle_{aa} = \int \phi_a(1)\left(\frac{1}{r_{12}}\right)_{\text{av. over } 2} \phi_a(1)\mathrm{d}v_1 \qquad . \quad . \quad . \quad (17)$$

$$\left\langle\frac{1}{r_{e1}}\right\rangle_{aa} = \int \phi_a(1)\frac{1}{r_{e1}}\phi_a(1)\mathrm{d}v_1 \qquad . \quad . \quad . \quad . \quad . \quad (18)$$

$$\left\langle\frac{1}{r_{e1}}\right\rangle_{ab} = \int \phi_a(1)\frac{1}{r_{e1}}\phi_b(1)\mathrm{d}v_1. \qquad . \quad . \quad . \quad . \quad . \quad (19)$$

Eqn. (14) and (15) show, as stated earlier, that inter-electronic Coulomb repulsions chiefly affect β, and internuclear repulsions chiefly affect E_0. Since $\left(\frac{1}{r_{12}}\right)_{\text{av. over } 2}$ is more or less constant in the region between the nuclei, it is quite consistent with our previous neglect of overlap integrals to put all the integrals of types (16) and (19) equal to zero. In that case, which is certainly too severe an approximation, all the resonance integrals (14) would be equal. But the Coulomb terms would be far from equal, and by no reasonable approximation or neglect of terms could they be made even roughly equal. For the Coulomb integrals (17) are quite large, as a simple numerical calculation shows. Indeed (5) and (11) show that (17) is greater than one-half of the Coulomb repulsion term in atomic H^-, i.e. greater than

$$\int \phi_a^2(1)\phi_a^2(2)\mathrm{d}v_1\mathrm{d}v_2/r_{12}.$$

It is not practicable to give numerical values to the various integrals in (15); but one immediate conclusion to be drawn from this analysis is that Coulomb terms in MO theory are very sensitive to the number and arrangement of the nuclei. In particular on account of the more diffuse charge cloud affecting (17) differently in the two molecules, $E_0(H_3^+)$ is necessarily numerically greater than $E_0(H_2)$, so that the addition of a cation must be allowed for by a change in all the Coulomb terms. This change will be such as to increase the total energy and therefore reduce the binding energy. If the change is not made we must anticipate that our calculations will yield too great a binding energy. This is the origin of the apparently high affinity for additional atoms which the simpler forms of MO theory lead us to expect. Also, there is a characteristic difference between linear and equilateral H_3^+. For if we may put

$$\left\langle\frac{1}{r_{e1}}\right\rangle_{aa} \simeq \frac{1}{r_{ae}},$$

then

$$E_0(H_3^+) = E_0(H_2^+) - \frac{1}{2}\frac{1}{r_{ae}} + \frac{1}{2}\left\langle\frac{1}{r_{12}}\right\rangle_{aa}.$$

Now for the equilateral molecule $1/r_{ae} = 1/r_{ab}$, but for the linear molecule $1/r_{ae} = 1/2r_{ab}$. The differences in $\left\langle\frac{1}{r_{12}}\right\rangle_{aa}$ are considerably less than this, so that E_0 for the equilateral molecule is numerically greater than E_0 for the linear molecule. This gives us an explanation of the fact that the simple MO theory suggests a better binding when the nuclei are " bunched together " than when they are more spread out in a " linear " chain.

We do not wish to suggest that the values that we have used above for the various integrals are at all closely correct. Indeed, it is evident that they are not, for we know that in H_2^+, the effective nuclear charge

and internuclear distance are different from those for H_2. Thus, for example, it is not fair to give $\left\langle \frac{1}{r_{12}} \right\rangle_{aa}$ in (17) the same value both in H_2^- and in H_2. Also, on account of the different internuclear distances in H_2 and H_2^+ there are changes in $\frac{1}{r_{ab}}$ which must be comparable in magnitude with the Coulomb terms with which we have been mainly concerned; and as the changes are sometimes in opposite directions, it is impossible to be sure that the resulting alterations in the resonance integrals β may not actually outweigh the change in the Coulomb terms E_0.

But it seems to us, notwithstanding this and other similar related objections, that the argument which we have given throws some light on the nature of the difficulties that will be found when we try to compare the binding energies of systems such as R and RX^+. If our argument is valid, it implies, first, that the numerical values obtained in such calculations must be regarded as indicative of a general situation and not descriptive in any precise way of any actual one: and, second, that the whole MO theory will need considerable development if it is to be applied in any satisfying and consistent manner to yield conclusions which are numerically reliable.

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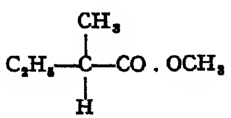
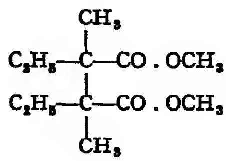
GENERAL DISCUSSION.

Mr. L. E. Sutton (*Oxford*) said: Prof. M. S. Kharasch and Prof. W. H. Urey (Chicago) have obtained evidence that free radicals are not flat, in the following two ways. One optical isomer of the compound (I) was treated with methyl radical to remove hydrogen. The substance (II) obtained as a product was optically active. Similarly, treatment of the active compound (III) with cobaltous sub-chloride * gave an active product (IV).



(I)



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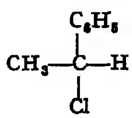
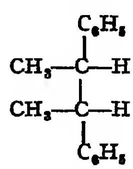


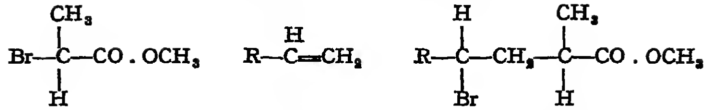
(III)



(IV)

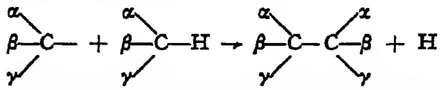
Secondly, a radical-type addition of an active bromo compound such as (V) to a 1-ene (VI) gives an active product of the type (VII). This contains one centre of activity created by the addition reaction; but the product will not be active unless the radical maintains its activity during addition.

* See papers by Kharasch, Urey, *et al.*, *J. Amer. Chem. Soc.*, and *J. Org. Chem.*



(V) (VI) (VII)

Dr. P. Goldfinger (*Brussels and Nancy*) said: An alternative mechanism involving plane free radicals would be



in which only the optical activity of one carbon atom is lost. It should not be too difficult to decide experimentally which of the two occur.

Mr. L. E. Sutton (*Oxford*), in reply, said: One way of deciding this point will be to compare the activity of the actual product of the reaction with the activity of a single optically isomeric species thereof. Prof. Kharasch and Prof. Urry are attempting the necessary resolution but it is proving difficult. If the activity of the actual product were half, or less than half, of the maximum possible value, the Kharasch and Urry test would be inconclusive unless independent evidence against the occurrence of the reaction postulated by Prof. Goldfinger were adduced. If, however, the actual activity were more than half the maximum, the validity of the test would be upheld.*

One objection to the postulated reaction is that because it involves the breaking of a C—H link to form a C—C link it would be endothermic by about 15 kcal./mole.

Dr. W. A. Waters (*Oxford*) (*communicated*): There can be little doubt of the planarity of free $\cdot CH_3$, but it does not follow that every other radical, $\alpha\beta\gamma C\cdot$; should be planar. Quite apart from steric blocking, such as that which has been indicated by Dr. Szwarc, a radical or a cation $[\alpha\beta\gamma C]^+$ will not be planar if it contains any angularly-disposed dipolar groups, such as CO—OEt, since these will interact so as to give the whole radical a tetrahedral configuration (though of course not that of the same group in H—C$\alpha\beta\gamma$).

The reactions which Dr. Sutton has reported can perhaps be explained in the same way as can the retention of optical activity of α-bromopropionic acid upon unimolecular hydrolysis.

Mr. T. L. Cottrell and Mr. R. E. Richards (*Oxford*) (*communicated*): We are of the opinion that Dr. Walsh has slightly over-emphasised the generality of his fundamental principle and its corollary. It is true, as pointed out by Mulliken [1] in 1937, that from general chemical considerations this principle is a reasonable one, and can interpret some experimental observations. It is certain, however, that other factors are also very important in determining the variations of bond type and strength in compounds and this detracts somewhat from the value of Dr. Walsh's principle as it stands.

There is no evidence that the chlorinated methanes, quoted as an example of the corollary, do in fact support it. The thermochemical argument suggesting that the C—H link increases in strength from methane to methyl chloride depends on the assumption of a decreasing C—Cl distance in passing along the series CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4. This is not observed; Sutton and Brockway [2] have stated that the C—Cl distance remains substantially the same in all these compounds. Furthermore, the C—H force constant, calculated by Linnett,[3] shows no significant

* cp. Brown and Chao, *J. Amer. Chem. Soc.*, 1940, **62**, 3439.
[1] *J. Physic. Chem.*, 1937, 41, 318.
[2] *J. Amer. Chem. Soc.*, 1935, 57, 473.
[3] *Trans. Faraday Soc.*, 1945, 41, 223.

cant variation from methane to chloroform. Fox and Martin state[4] that the stretching force-constant of the C—H links of methyl bromide is very close to that in methane. The force constants quoted by Duchesne[5] for the series of molecules CH_3Cl, CH_3Br, CH_3I, show a slightly increased value in passing from the chloride to the iodide, the opposite of the result expected on the basis of Dr. Walsh's corollary. These latter results cannot be regarded as completely reliable, however, since the vibration frequencies were obtained from the Raman effect on the liquids, and not from the vapours. From this it must be concluded that there is no experimental evidence to show that an increase in the C—H stretching force-constant occurs in the halogenated methanes. The finding of Bak[6] that the methyl group in methyl chloride is flatter than in methane is not confirmed by more recent measurements of Gordy, Simmons and Smith.[7] They find that if a tetrahedral arrangement is assumed for methyl chloride, with the CH distance as in methane, the moment of inertia from microwave spectrum yields a C—Cl distance of 1·78 A., in good agreement with the electron diffraction measurements.[3] Also, the CH distance in methyl chloride found by Bak seems to be rather short (1·04-1·05 A.) in view of the force constant. The C—H link of methyl fluoride has a force constant appreciably lower than in methane, which appears to be inconsistent with the increased *s* character of these bonds expected from the corollary.

The application of the fundamental principle to predict the stretching force-constant of the CH links of formaldehyde gives an answer which disagrees with the experimental results. The polar carbonyl group of formaldehyde causes the carbon atom to become more electronegative towards the hydrogen atoms so that from the fundamental principle, the *s* character of the C—H links should increase. This should lead to an increase in the C—H force-constant, which although off-set to some extent by the increased polarity of the link, should at least be equal to, or greater than, that of methane. The C—H force-constant of formaldehyde is in fact very much lower than in methane, lying between the values 3·7 and 4·3 $\times$ 10[5] dynes per cm., according to the force field used.[3, 8] The force-constant of the C—H links of methane is given by Herzberg,[9] as 5·04, by Linnett[3] as 4·97, and by Fox and Martin[4] as 5·04, all in units $\times$ 10[5] dynes per cm. The value of 4·79 given by Dr. Walsh is probably too low.

As pointed out by Dr. Walsh, his fundamental principle suggests that the HCH angle of ethylene should be slightly greater than 120°, but it is in fact found[10] that the angle is less than 120°.

The examples quoted above suggest that the factors involved in bond strengths are very complicated, and cannot be completely summarised in a single generalisation such as that given by Dr. Walsh. The application of the principle to the prediction of data for other molecules or radicals must therefore be made with great caution.

Dr. E. Warhurst (*Manchester*) said: I should like to point out that Table II of Dr. Walsh's paper indicates that for C—H bonds in the series of molecules CH_4, C_2H_4 and C_2H_2, the bond strength increases with increase in *s* character. How does Dr. Walsh reconcile this with Pauling's views which entail a slight decrease in bond strength with increase in *s* character along the series $sp^3 \rightarrow sp^2 \rightarrow sp$?

This contradiction could be avoided by adopting the view that the covalent bond strength actually does decrease with increase in *s* character,

[4] *Proc. Roy. Soc. A*, 1940, 175, 208.
[5] *Nature*. 1947, 159, 62.
[6] *J. Chem. Physics*, 1946, 14, 698.
[7] *Physic. Rev.*, 1947, 72, 344.
[8] Conn, *Trans. Faraday Soc.*, 1945, 41, 236.
[9] Herzberg, *Infra-red and Raman Spectra*.
[10] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, 59, 1223. Thompson, *Trans. Faraday Soc.*, 1939, 35, 697.

but, in the above series of molecules, this factor is more than offset by the increase in bond energy resulting from an increase in $C^{-}H^{+}$ ionic character of the bonds along the series, the changes in radical resonance energy, which would also lower the bond strength, being too small to influence the sign of the trend in bond strength.

Dr. A. D. Walsh (*Cambridge*) (*communicated*): I agree with Mr. Cottrell and Mr. Richards that the factors involved in bond strengths are many. That should have been plain, since my paper was stated to be a translation into other terms of an earlier approach [11] and in this complementary paper I made very clear the complexity of the factors involved (cf. also [13]).

Mr. Cortrell and Mr. Richards say that a decreasing CCl distance in the series CH_3Cl . . . CCl_4 is not observed. But Sutton and Brockway [11] give $r(\text{CCl})_{CH_3Cl} = 1{\cdot}77 \pm 0{\cdot}02$ A. as compared with $r(\text{CCl})_{CCl_4} = 1{\cdot}760 \pm 0{\cdot}005$ A.[15] or $1{\cdot}749$ A.[16] That is part of the justification for saying [1] that there is a probable decrease from CH_3Cl to CCl_4. Further justification comes from the facts that successive Cl substitution for CH_3 linked to a central atom X (where X may be Sn, As or N) probably leads to successive reduction of the XCl length;[17] and that, with the chlorosilanes, the SiCl distances tend to be larger the fewer the Cl in the molecule.[18] To quote the paper by Sutton and Brockway [14] as in some way providing evidence against these suggestions is misleading. In fact, those authors say, "A simple theoretical calculation may be made of the effect of the repulsive forces between the Cl atoms.'. . . It is found that there should be an increase in the bond distance from CH_2Cl_2 to CCl_4. . . . Since the observed bond distances show that such an increase lies outside the range of experimental error *but that a small decrease is possible*, it is evident either that the repulsive forces are less effective . . . than we have assumed or that *there is some compensating effect tending to make the CCl distance shorter as more Cl atoms are introduced into the molecule, such as some kind of mutual interaction of the bonds.*" The italics are mine. Here, at an early date, is recognition of just the effect of which my work has given an interpretation. There is no doubt of the importance of the Cl—Cl repulsive forces (witness the moving-apart of the Cl atoms as we pass from CCl_4 to $CHCl_3$ to CH_2Cl_2).[11] The smaller the central atom (X) the greater these repulsive forces, so that the length decreases with successive Cl substitution may well be less when X is C than when X is, say, Sn. It may, of course, be that further experimental data will show that other factors more than offset the electronegativity effect in some of the chloro-methanes (cf. [19]) but the effect is clearly there and is important.

As regards formaldehyde, I have made suggestions elsewhere [13] about its structure that sufficiently emphasise the complexity of the problem. These revise, in certain particulars, earlier remarks.[11] As regards ethylene, I have already pointed out that the effect of the π bond is to provide a factor offsetting that embodied in my corollary. Similarly, the difficulties with molecules such as methyl fluoride have already been mentioned.[11] In all these cases, then, the complexity of the factors influencing the strengths of bonds has been stressed. My present paper is certainly not supposed to be a single panacea for all the ills of bond strength estimates. Nevertheless the ideas contained in it are useful ones. They will be all the more so, if they can be made quantitative and if other,

[11] Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60; see also [12].
[12] Walsh, *J. Chem. Soc.* (in press).
[13] Walsh, remarks on paper by Dyne and Style (this Discussion, p. 159).
[14] Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473.
[15] Pauling and Brockway, *J. Chem. Physics*, 1934, **2**, 867.
[16] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 2684.
[17] Skinner and Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.
[18] Livingston and Brockway, *J. Amer. Chem. Soc.*, 1946, **68**, 719.
[19] Duchesne (in course of publication).

possibly offsetting, factors can also be analysed[20] and made quantitative. My papers so far are to be regarded as an attempted step on the way towards this ultimate goal.

I was very interested to learn of Mulliken's remarks. I had not previously known of them. Mulliken, however, developed the fundamental principle much less than I have done.

In answer to Dr. Warhurst, the strength of bonds formed from carbon orbitals *increases* along the series, p, sp^3, $s\,p^2$, sp. The data of Table II of my paper are too complete and consistent to be overthrown in their trend. Pauling's treatment[21] commences by ascribing to a $2p$ wave function a bond-forming power $\sqrt{3}$ times that of a $2s$ wave function. This ascription rests on considerable approximations. It neglects the energy difference of the $2s$ and $2p$ wave functions and the difference between the radial parts of those functions. In other words it assumes that bond-forming power depends only on the power of overlap. But another very important factor is the electronegativity of the overlapping orbitals.[12, 22] Pauling recognised this factor in his "Rule 6"—"*Of two eigenfunctions with the same dependence on θ and ϕ, the one with the smaller mean value of* r, *that is, the one corresponding to the lower energy level for the atom, will give rise to the stronger bond*"—but thought it small. It is this neglect which seems to be responsible for the apparent disagreement between Pauling's figures of bond-forming strength and the CH bond strengths. The electronegativity factor compensates the overlap factor, increasing the bond-forming power of the $2s$ relative to that of the $2p$ wave function. If one took the ratio of the bond-forming powers of the $2p$ and $2s$ wave functions as approximately 1 instead of $\sqrt{3}$, then, relative to the "strength" of the s orbital taken as 1·000, one finds the following "strengths": pure p, 1·000; tetrahedral, 1·366; trigonal, 1·394; digonal, 1·414. This gives the order expected from Table II of my paper and gives the strongest bond-forming powers to the digonal valences, as required, but the procedure is not very satisfying.

The increase in bond strength along the series $(CH)_{CH\ radical}$, $(CH)_{CH_4}$, $(CH)_{C_2H_4}$, $(CH)_{C_2H_2}$ cannot be explained by increase of polarity in that series. Several theoretical viewpoints expect and many experimental facts indicate that bond strengths (not necessarily dissociation energies) *weaken* with increase of polarity.[11, 12, 23, 24, 25]

Mr. G. Porter (*Cambridge*) said: I was very interested in Dr. Walsh's suggested figure of 115 kcal. for the CH bond strength in methylene, leading to the conclusion that the triplet state may be the one of lowest energy, as this is in agreement with the free-radical nature of methylene described in our paper. Unfortunately the figure is derived from emission spectra data which are unreliable not only because, as Dr. Walsh is careful to point out, the identification of the emitter is not certain, but also because this spectrum is observed only in comets and discharge tubes both of which would be expected to produce highly excited molecules with very different bonding from the ground state. The spectrum obtained by Mme. Herman[26] could only be explained in this way.

A second point is that if we accept a figure for CH bond strength which makes the promotion energy to the triplet state small, or negative, it is difficult to see how we can explain the results of Bawn and Dunning[27] who require a minimum of 27 kcal. for this transition to account for the

[20] Some progress has already been made here: see ref.[3]

[21] Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367; *Nature of the Chemical Bond*, 2nd edn. (Cornell, 1940), pp. 78-87.

[22] Gordy, *J. Chem. Physics*, 1946, **14**, 305.

[23] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 56.

[24] Walsh, *Ibid.*, 1947, **43**, 158.

[25] Walsh, *Ann. Reports* (in press).

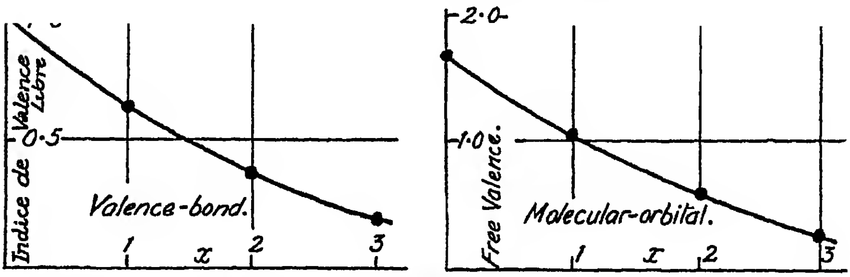
[26] Herman, *Compt. rend.*, 1946, **223**, 280.

[27] Bawn and Dunning, *Trans. Faraday Soc.*, 1939, **35**, 880.

observed sodium D radiation in the reaction of sodium with methylene halides.

Mde. A. Pullman (*Paris*) (*communicated*): The great difference between the experimentally-established value of the resonance energy of the benzyl radical and that calculated by Pauling and Wheland by the v.b. method may be, at least partially, attributed to the fact that in the calculations carried out by these authors account has been taken only of the unexcited structures. Even if only a part of the possible excited structures is introduced in the secular equation (see A. Pullman, this Discussion) there is a considerable increase in the resonance energy of the free radical. In our treatment in which five singly-excited structures have been introduced, the resonance energy has been raised by $0{\cdot}092\alpha$. This represents (if we take Pauling's value of 32·2 kcal. for α) nearly 3 kcal. and brings the theoretical value of the resonance energy much nearer the experimental one. The agreement may be expected to be still better if all the excited structures are taken account of.

Prof. C. A. Coulson and Miss J. Jacobs (*London*) (*communicated*): The characteristic property of conjugated free radicals, that the free valence is not even approximately localised on one carbon atom, is well exhibited by the series of radicals CPh_xH_{3-x}, where $x = 0, 1, 2, 3$. When $x = 0$ we have the methyl radical CH_3 in which the free valence is confined



to the carbon nucleus; but with increasing phenylation ($x = 1$ is benzyl and $x = 3$ is triphenylmethyl) there are more alternatives for the odd electron and consequently the free valence at the central carbon would be expected to get steadily smaller as x increases. The method of molecular orbitals does not speak of different positions for the unpaired electron, but [28] of a free valence number F for each of the carbon atoms, defined in terms of the total bond number N of the atom by the relation:

$$F = N_{max} - N = 4{\cdot}680 - N.$$

We have calculated values of the bond orders, and hence deduced the free valences, at all the carbon nuclei of this series of radicals. Full results will be published later, but they are most simply summarised in the table below, where, for different values of x, we show the corresponding free valence number of the central carbon.

$x =$	0	1	2	3
$F =$	1·68	1·04	0·61	0·27

This set of values shows very clearly how by increasing the degree of conjugation the free valence of the methyl carbon is steadily diminished.

Substantially similar results to these are found by Madame Pullman [29] for the same set of radicals, using the valence-bond method. When the two sets of values are shown, as in the figure, plotted with their scales adjusted to make the curves approximately the same size, it is seen that there is very close agreement between them. This agreement justifies us in believing that they do both correspond to the facts.

[28] Coulson, this Discussion, p. 9. [29] Pullman, this Discussion, p. 26.

Dr. R. Daudel (*Paris*) said: It is clear that the free valence is not a specific property of free radicals. In the valence-bond method the existence of free valence can arise from two different effects.

First, the presence of an *odd* number of electrons which is really the specific character of free radicals. This is the case in C_3H_5, for example, as we can see in this formula: $=\!-\cdot$.

Secondly, the necessity of introducing "excited" formulæ which can appear both in the case of usual molecules and in the case of free radicals.

For C_3H_5 we can neglect the "excited" formulæ so the free valence number comes only from the presence of an odd number of electrons, and the sum of free valence numbers is unity. For naphthalene the free valence comes only from the "excited" formulæ, but the sum of free-valence numbers has about the same value (1·114).

For the naphthyl radical, the free valence comes both from the presence of an odd number of electrons and from the necessity of introducing "excited" formulæ.

Dr. E. Warhurst (*Manchester*) (*communicated*): In view of the discussion concerning the magnitude of α, the exchange energy between neighbouring carbon atoms, it seems opportune to draw attention to a considerable amount of evidence which indicates strongly that Pauling's original value of $\sim$ 32 kcal./mole is much too low. One method which has been used for the evaluation of α from empirical data consists in equating the solution of the secular equation to the so-called empirical resonance energy obtained from heats of formation or combustion, i.e. the difference between the actual heat of formation of the particular molecule and that of a particular bond assignment. It is clear that the use of bond-energy terms for C—C and C=C bonds in calculating the heat of formation of the molecule with the particular bond assignment gives the energy of a structure for which all the C—C bond lengths are 1·54 A. and all the C=C bond lengths are 1·34 A. Such a structure is clearly not one of the canonical structures contributing to the actual state of the molecule. The energies of extension of C=C bonds and compression of C—C bonds which are necessary to arrive at a structure in which all the bonds are equal to the corresponding bond lengths in the actual state of the molecule have been neglected. This has been pointed out previously, in particular by Penney, Lennard-Jones, Coulson and Mulliken. In a similar way the evaluation of α from heats of hydrogenation involves energy terms due to changes in bond lengths which are often overlooked.

These energies of compression and extension can easily be evaluated by means of Morse curves and turn out to be quite considerable in magnitude and, when incorporated into a number of thermochemical cycles, result in estimated values of α which are much greater than 32 kcal. per mole. Values for the resonance energies of unsaturated hydrocarbons are also much increased when allowance for this factor is made. The different cycles which enable a calculation of the magnitude of α are summarised briefly below, together with the resulting value of $\alpha_{1\cdot39}$, i.e. the value of α at the benzene carbon-carbon distance of 1·39 A.

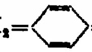
(i) Neglecting coulombic interaction and assuming $\alpha_{1\cdot39}$ is equal to the energy of "the second-half" of a double bond for the internuclear separation 1·39 A., the heat of hydrogenation of a simple mono-olefine provides a means of a rough estimate of $\alpha_{1\cdot39}$. Ethylene and cyclohexene give values of 65 and 69 kcal./mole, respectively.

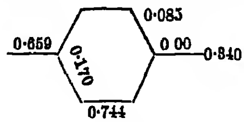
(ii) The heats of hydrogenation of benzene and cyclohexene taken in conjunction with the solution of the secular equation for benzene gives $\alpha_{1\cdot39} = 64$ kcal./mole.

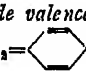
(iii) The empirical resonance energy, obtained from heats of combustion of an aromatic hydrocarbon for which all bond lengths may be taken to be 1·39 A., when corrected for extension and compression of bonds and taken in conjunction with the solution of the secular equation enables

$\alpha_{1.39}$ to be evaluated. By this method benzene and naphthalene give $\alpha_{1.39}$ = 67 and 70 kcal./mole, respectively.

These values may be somewhat high due to the neglect of small differences in bond energy for sp^3 and sp^2 hybridisation. The results as a whole, however, indicate strongly that a value for $\alpha_{1.39}$ considerably greater than 32 kcal. mole, perhaps twice as large, should be adopted. When the compression and extension energies are allowed for the true resonance energy of benzene becomes 70-74 kcal./mole and that of naphthalene $\sim$ 144 kcal. mole.

Dr. R. Daudel (*Paris*) (*communicated*): The molecular diagram [30] of the $CH_2=$$=CH_2$ molecule studied by Szwarc is



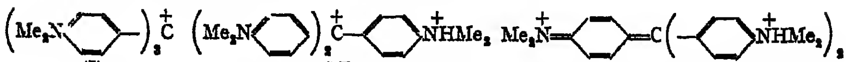
This diagram shows two very high *indices de valence libre* and is in good agreement with the tendency of the $CH_2=$$=CH_2$ molecule to react by polymerisation.

Dr. G. Salomon (*Delft*), said: The assumption that the non-planar configuration of hexaphenylethane contributes essentially to the formation of the triphenylmethyl radical finds further support in the 1942 paper of Ziegler. The frequency factor in the dissociation reaction is, for certain tetraphenylalkyl ethanes, as high as 10^{18} sec.$^{-1}$. The fact that this probability of dissociation is 10^5 times higher than the theoretical value suggests the existence of a transition state, which is sterically preferred and therefore more probable than the initial state.

The occurrence of the *p*-xylyl radical as an intermediate in reactions involving cyclo-octatetraene is not substantiated by experiments. Reppe has suggested the intermediate formation of 1, 2-4, 5-dimenthylene-cyclohexadiene-2, 5, which links up with certain results in terpene chemistry. The polymers from cyclo-octatetraene are essentially of low degree of polymerisation while the interesting compound obtained by Szwarc should resemble cuprene.

Dr. M. J. S. Dewar (*Maidenhead*) (*partly communicated*): Has it been definitely established that the decomposition of toluene is not a chain reaction? Has Dr. Szwarc resolved the discrepancy between his results and those of Butler and Polanyi [31] on the thermal decomposition of benzyl iodide, which indicated a resonance energy of $\sim$ 10 kcal. for the benzyl radical?

Crystal Violet (I) is converted by acid first into the cation (II) with the green colour characteristic of analogous diphenylmethane dyes and then into the pale quinonoid ion (III).



(I) (II) (III)

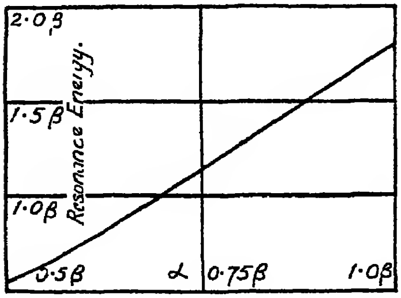
These colour changes establish that in (I) all three benzene rings are conjugated with the central carbon. Similar resonance will presumably occur also in the radical.

Steric strain must undoubtedly play an important part in stabilising triphenylmethyl, and it will also reduce the resonance energy by decreasing the exchange integral between each ring and the central carbon. In the figure the resonance energy, calculated by the molecular-orbital

[30] Obtained by Chalvet, Henriet and Lesein (valence bond method), *Compt. rend.*, 1947, **225**, 1010.

[31] *Trans. Faraday Soc.*, 1943, 39, 19.

method, is plotted against the value (α) of this exchange integral. It will be noticed that even for quite large decreases in α, the resonance energy remains considerable. It is difficult to estimate α in terms of the angle (θ) through which each benzene ring is twisted, but analogy suggests that $\alpha \simeq \beta \cos^2\theta$. For $\theta = 30°$ this gives $1{\cdot}13\beta$ for the resonance energy, compared with $0{\cdot}72\beta$ in benzyl.



The steric effects of *ortho* substituents in dimethylaniline do not imply that exact coplanarity is necessary for resonance. Considerable energy is required to alter the hybridisation of the nitrogen in aniline from sp^3 to the sp^2 necessary for mesomerism; therefore quite a small fractional decrease in the resonance energy may make the unconjugated sp^3 state of aniline the more stable. No such effect can occur in triphenylmethyl.

Prof. E. C. Baughan (*Shrivenham*) said: There is one point I would like to make in comment on Dr. Szwarc's paper. In the earlier work by Polanyi and his co-workers [12] on the aliphatic hydrocarbons, bond energies were established *first* by calculating substitution energies, i.e. the energies of the reactions

$$RH + Y \rightarrow RY + H$$

(where Y may be, say, CH_3, OH, Br, I, etc.) for each radical R, and *then* translating these into bond dissociation-energies by using the absolute value for any one bond (e.g. the R—I bond). The substitution energies follow directly from thermochemical data plus the heats of a few simple reactions like $H + I \rightarrow HI$, errors in which do not affect *differences* in substitution energies as between different R's. Some very thorough recent work in Amsterdam [33] enables one to collect some substitution energies for benzyl and triphenyl methyl radicals; I hope to submit these for publication soon. In particular, it appears that the substitution heat of H by CH_3 or C_6H_5 is very much the same if $R = CH_3$ or $C(C_6H_5)_3(Z)$. In other words the Z—H, Z—CH_3, Z—phenyl bonds are weaker by a constant amount than the corresponding CH_3—H, CH_3—CH_3, CH_3—phenyl bonds, and this weakening amounts to about 28 kcal. (based on Bent and Cuthbertson's [34] value for the heat of the reaction, $Z_2 + H_2 \rightarrow 2ZH$, Ziegler's [35] value for $Z_2 \rightarrow 2Z$, and the Polanyi value [32] for the CH_3—H bond).

This fact suggests strongly that the resonance energy of the triphenylmethyl radical is about 28 kcal. Comparing this with that advocated by Szwarc for the benzyl radical (24 kcal.) I would like to ask Dr. Szwarc if this small difference fits in with the great difference in stability between benzyl iodide and Z—I, which is known to dissociate to about 20 % into free radicals even at room temperature in solution.[36] Possibly his steric interpretation is also valid here—it is at any rate known that the substitution of H by Br is *less* exothermic for Z than for benzyl: [37] the directly-determined values of the benzyl-iodide bond show considerable disagreement.[31, 38]

[32] Butler and Polanyi, *Nature*, 1940, 146, 121; *Trans. Faraday Soc.*, 1943, 39, 19. Baughan and Polanyi, *Nature*, 1940, 146, 685.
[33] Coops, Mulder, Dienske and Smittenberg, *Rec. trav. chim.*, 1946, 65, 170.
[34] *J. Amer. Chem. Soc.*, 1936, 58, 170.
[35] Ref. 21 in Dr. Szwarc's paper
[36] Gomberg, *Ber.*, 1902, 35, 1826.
[37] Magee and Daniels, *J. Amer. Chem. Soc.*, 1940, 62, 2832.
[38] Szwarc and Horrex, *Nature*, 1946, 158, 592; Butter and Polanyi, ref. [16].

Dr. M. Szwarc (*Manchester*) (*communicated*) : I would like to give two arguments in reply to Dr. Dewar's question : has it been established that the decomposition of toluene is not a chain reaction ? Jost and Müffling [39] investigated the thermal decomposition of a number of aliphatic and aromatic hydrocarbons. They found that the addition of $Hg(CH_3)_2$ accelerates the decomposition of aliphatic hydrocarbons (i.e. initiates the chain), while it was without any effect on the rate of decomposition of toluene. They take this as a proof that the thermal decomposition of toluene is not a chain reaction.

I found that the products of pyrolysis of toluene are H_2, CH_4, benzene and dibenzyl. The last product is formed in the proportion corresponding to one mole of dibenzyl for each mole of H_2 or CH_4. I can visualise only one chain mechanism which accounts for these facts, i.e.

$$C_6H_5 . CH_3 \rightarrow C_6H_5 . CH_2 + H \quad . \quad . \quad (1)$$
$$C_6H_5 . CH_3 + H \rightarrow C_6H_5 . CH_2 + H_2 \quad . \quad . \quad (2)$$
$$C_6H_5 . CH_3 + C_6H_5 . CH_2 \rightarrow (C_6H_5 . CH_2)_2 + H. \quad . \quad (3)$$

The reactions (2) and (3) represent chain propagation. Reaction (3), however, is endothermic to the extent of $R + 5$ kcal. ($R =$ the resonance energy of the benzyl radical), and therefore such a chain mechanism is ruled out.

Answering his second question concerning the apparent discrepancy between the results obtained by Butler and Polanyi (pyrolysis of benzyl iodide) as compared to those obtained by the pyrolysis of toluene, I would like to point out that their value results from the use of an expression $k = 10^{13} . e^{-E/RT}$. A reinvestigation of the pyrolysis of benzyl iodide by C. Horrex and myself showed definitely that this reaction is not a unimolecular reaction and that the C—I bond is weaker than that reported by Butler and Polanyi by at least 4 kcal. (and probably by 7 kcal.). I hope that the work now in progress will enable us to determine the C—I bond energy in benzyl iodide.

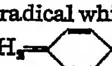
The remark of Prof. Baughan is extremely interesting. It is quite probable that the steric effect is responsible for the peculiar behaviour of triphenyl methyl iodide. We intend to investigate the heat of the reaction

$$2 \, Ph_3CI \rightleftharpoons Ph_3C . CPh_3 + I_2$$

and thus to find the energy of the C—I bond in this compound.

Calculations show that the energy of electrostatic interaction between a C—H dipole and the Ph—CH_3 dipole in *p*-xylene is of the order of 0·01 kcal. Therefore this interaction cannot account for the decrease of 2·5 kcal. in the C—H bond energy of *p*-xylene as compared with toluene and *m*-xylene.

The recent study by Mr. J. S. Roberts and myself of the pyrolysis of the three fluoro-toluenes gives a conclusive answer to the question how far the energy of the bond is influenced by the dipole interaction. The introduction of a strong dipole such as C—F in the *p*-, *m*- and *o*-position of the toluene molecule does not change the C—H bond energy by more than 0·35 kcal. at most. We are, therefore, on safe ground if we attribute the observed decrease of the C—H bond energy in *p*-xylene to the hyper-conjugation effect.

Dr. Dainton, F.S., and Mr. K. G. Ivin (*Cambridge*) (*communicated*) : Dr. Szwarc has drawn attention to the existence of the *p*-xylyl diradical which stabilises itself by rearrangement to the non-benzenoid form CH_2  CH_2, which, though stable in the gas phase, undergoes immediate polymerisation when condensed. Presumably polymerisation is not observed in the gas phase because monomer-diradical collisions are infrequent at the

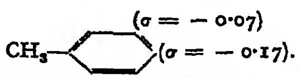
[39] Jost and Müffling, *Z. Elektrochem.*, 1941, 47, 766.

low gas concentrations employed, and most of the diradicals are lost by stabilisation or at the wall before the polymerisation can be initiated. If this is true, the *p*-xylyl diradical shows similar behaviour to the vinyl sulphinyl diradical. We have recently been studying the reactions between hydrocarbons and sulphur dioxide under the influence of ultraviolet light, and have concluded that vinyl sulphinyl diradicals, written provisionally as $—\overset{\overset{\large R}{|}}{C}H—CH_2—SO_2—$, are the first products of bimolecular interaction of an olefine and an electronically-excited sulphur dioxide molecule. Such a radical may be stabilised by intramolecular rearrangement, involving migration of a hydrogen atom, to a vinyl sulphinic acid, e.g. $RCH{=}CH\,.\,SO\,.\,OH$. The life of the diradical before rearrangement is considered to be greater than the interval between collisions of the diradical and reactants which lead to polymerisation in the liquid phase, but shorter than the corresponding interval in the gas phase. Consequently, the products of the gas-phase reaction are predominantly sulphinic acid with only traces of copolymer, whilst in the liquid phase the product appears to be exclusively polysulphone. It should be mentioned that the liquid-phase reaction between sulphur dioxide and olefines is probably complicated by the formation of π-complexes (see comment on Dr. G. Salomon's first paper).

Prof. C. C. Price (*Notre Dame*) said: The considerably greater reactivity of *p*-xylene as compared to *m*-xylene and to toluene in thermal decomposition to a hydrogen atom and benzyl radical

$$ArCH_3 \xrightarrow{\text{heat}} ArCH_2^{\bullet} + H^{\bullet}$$

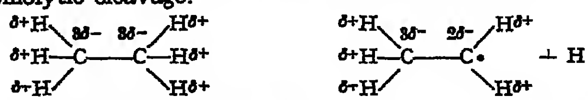
discussed by Dr. Szwarc, as well as the increase in stability in paraffinic radicals with increasing substitution, has been interpreted in terms of hyperconjugation. It seems possible to understand these observations at least as well in terms of simple electrical interaction. If we consider the effect of a methyl group in toluene on the electron distribution in the benzene ring, estimates in terms of Hammett's σ constant [40] and by Ri and Eyring [11] indicate a considerably greater negative charge for *para* than *meta*:



If we now place a methyl group at the *para* position we may represent the electrical distribution qualitatively as follows: [41]

Homolytic cleavage of the C—H bond in *p*-xylene will thus have an additional factor in its favour involving diminution of the coulombic potential energy by decreasing the magnitude of negative charge on adjacent carbon atoms.

Similarly, if we compare ethane with the ethyl radical, we see that there has been a decrease in negative charge on adjacent carbon atoms during homolytic cleavage.



[40] Hammett, *Physical Organic Chemistry* (McGraw-Hill, New York, 1940).

[41] Ri, and Eyring, *J. Chem. Physics*, 1940, **8**, 433.

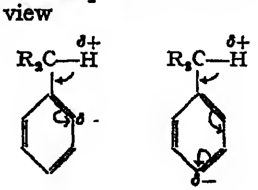
[42] The author cannot accept the theoretical assignment of the C—H dipole with the hydrogen negative as presented by Prof. Coulson and Dr. Walsh and prefers the very generally accepted view that the hydrogen is negative.

For removal of the tertiary hydrogen atom from *iso*butane, the magnitude of the change should be roughly three-fold greater.

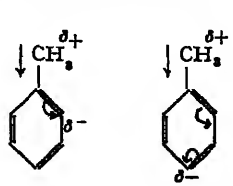
It thus appears possible to account for the effect of an alkyl group in increasing the relative stability of hydrocarbon free radicals in terms of a simple coulombic interaction rather than by hyperconjugation.

The much greater stability of the *tert*-butyl cation as compared to the methyl, ethyl and *iso*propyl cations can easily be accounted for on the same basis. The much greater magnitude of the stabilisation in the cation series as compared to the free-radical series would then be due to the fact that, whereas in the radical case we remove only a fractional electronic unit of charge from the carbon in question, in the ionisation of the radical to a cation, we remove an electron charge some ten-fold or more greater.

Dr. W. L. G. Gent (*London*) said: The view, expressed by Prof. C. C. Price, that in the *p*-xylene molecule the polarity within the methyl groups is $C^{\delta-}—H^{\delta+}$ cannot be doubted since the electric moment of toluene (+ 0·4 D.) has its positive pole at the methyl group.[43] There is good reason, however, for believing that the polarity is not in conflict with the reverse arrangement found in aliphatic C—H bonds.[44, 45] It is a convenient fiction to express the molecular electric moment as the sum of intrinsic bond moments, induced moments and mesomeric moment, so that in the case of toluene if $\mu(H—C) = -0{\cdot}3$ D. $= \mu(C_6H_5 - CH_3)$ then, without allowing for induction, there must be a mesomeric moment of about + 0·7 D., the net fractional charge on the hydrogens of the methyl group then being δ^+. This is of the same order as the mesomeric moment in the halogens[46] and is in accord with the chemical behaviour of toluene (and *p*-xylene). That such a moment exists is implied by the mechanism (I) invoked[47] to explain the order of reactivity of *p*-alkyltoluenes. In the writer's view



(I)



II

the tendency to mesomerism of the phenyl group is fostered by the large polarisability of alkyl groups[48] resulting in an inductive effect operative in a direction towards the nucleus (II).

Such an effect would explain the order of electric moments toluene < ethylbenzene < *iso*-propylbenzene < *tert*-butylbenzene[49] and somewhat resemble the explanation of mesomerism in the halogenobenzenes suggested by Bennett.[48] Under the influence of electrophilic reagents or in an excited state it might be expected that the Baker-Nathan mechanism

[43] Williams, *Physik. Z.*, 1929, 30, 391.
[44] Coulson, *Trans. Faraday Soc.*, 1942, 38, 433.
[45] Gent, *Nature*, 1946, 158, 27.
[46] Groves and Sugden, *J. Chem. Soc.*, 1937, 1992.
[47] Baker and Nathan, *ibid.*, 1935, 1844.
[48] Bennett, *et al.*, *ibid.*, 1933, 261, 1112 ; 1935, 1827.
[49] Ingold, *Chem. Rev.*, 1934, 159, 238.

(I) will supervene giving an even more positive character to the hydrogen atoms.[50]

Dr. W. A. Waters (*Oxford*) said: The time seems to have arrived when we should distinguish clearly between the two objects of theoretical chemistry: (*a*) the interpretation of molecular structure, and (*b*) the explanation of chemical reactivity, and see that our modes of formulating mathematical results concerning (*a*) are not tending to suggest fallacious conclusions concerning (*b*).

This distinction becomes most important when we consider olefinic and aromatic substances. "Double-bond character" is purely a structural term, and it need not be related simply to the type of reactivity which the organic chemist terms "unsaturation," i.e. the formation of addition compounds. For instance the S=O bond of sulphoxides (in which *d* electrons are concerned) is *not* unsaturated.

This distinction is easily overlooked when we talk of π-bond *formation*, and it is most unfortunate that the formulators of π-bonds have used Sidgwick's arrow symbol $\overset{C}{\underset{C}{\|}} \rightarrow X$ which indicates a process rather than a structure. For instance, whatever may be the *structure* of ethylene oxide, it is quite certain that it can *not* be made by the process of adding an atom of oxygen to a molecule of ethylene; it can only be prepared by making the dipolar structure $\underset{\diagdown O^-}{CH_2}\text{——}\overset{+}{C}H_2$, e.g. by treating ethylene chlorohydrin with caustic alkali. Again, the ethylene oxide ring is always broken unsymmetrically: we cannot remove oxygen from it in the way that we can remove oxygen from $(CH_3)_3N\rightarrow O$.

For the same reason, Dr. Dewar's paper may tend to give us a very false impression concerning unsaturation. Though it is an attractive theory to compare structurally a pair of unshared *p* electrons, as in $(CH_3)_3N$:, with a pair of π-electrons, as in ethylene, yet their reactions are, even qualitatively, very different.

Compounds with unshared *p* electrons are all potentially *basic*: they can pick up *any* electrophilic group, and react readily with H—Br, H—OH, $(CH_3)_3C$—Cl, CH_3—I, etc., at rates which depend upon their ease of cation release, but they do not react with the molecules of the halogens to form salts. Compounds with π-electron bonds, however, are not, in general, basic. They do not easily pick up H^+ from acids, or react with alkyl halides, except in the presence of the most powerful catalysts, yet they react quite easily with halogen molecules, Cl—Cl, or Br—Br, which have much stronger covalent bonds than H—Br or CH_3—I. It is significant too that electrically unsymmetrical olefines like $Me_2C=CH_2$ often react more rapidly with halogens than symmetrical olefines.[51] Again whilst bases such as $(CH_3)_3N$: do not react with free atoms, unsaturated compounds very readily add on another atomic nucleus *plus* one more electron, again by unsymmetrical attack at one of the carbon centres.

These examples serve to show that the reaction *processes* are very different, though in the case of bromine addition to olefines there is certainly very strong experimental evidence to justify the view that a polar *structure* $(CH_2=CH_2, Br)^+$ is formed. To-day it has been shown[52] that much of the evidence that has been adduced in support of the old Noyes-Lowry theory of the existence of free bromine cations, Br^+, is not conclusive, and really our experimental evidence of the polar nature of the bromination of ethylene in solution amounts to no more than recognition

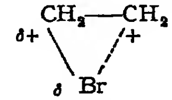
[50] Baker, *J. Chem. Soc.*, 1939, 1150.
[51] Ingold and Ingold, *ibid.*, 1931, 2354.
[52] Robertson and Waters, *ibid.*, 1947, 492.

of the fact that the primary reaction is either the bimolecular process,

$$Br\text{—}Br + CH_2{=}CH_2 \longrightarrow Br^- + Br\text{—}CH_2\text{—}CH_2^+,$$

or else the *ter*molecular process,

$$2Br_2 + CH_2{=}CH_2 \longrightarrow (Br_3)^- + Br\text{—}CH_2\text{—}CH_2^+.$$



(*A*)

In the cation $(Br\text{—}CH_2\text{—}CH_2)^+$ there is of course some electron interaction between the bromine atom and *both* carbon centres, and the π-bond formulation may perhaps be better than the formulation (*A*) in which we vaguely try to indicate electrostatic interaction between the $\overset{+\longrightarrow}{C\text{—}Br}$ dipole and the adjacent $\overset{+}{C}$ pole.

However, if we are to attempt to predict chemical reactivity by consideration of structural formulæ, the critical point that has to be decided is whether or not we are justified in taking note of the energy level of our cation $(Br\text{—}CH_2\text{—}CH_2)^+$ in estimating activation energies.

I would suggest that the essential difference between the chemical reactivity of the unshared *p* electrons of a base and that of the π-electrons of an unsaturated substance lies in the fact that their reactions, whilst both bimolecular, have very different critical transition states. That of the base is a linear system of three points of polarisation (*B*)

$$\overset{\delta-}{(CH_3)_3N} \;.\;.\;.\; \overset{\delta+}{CH_2} \;.\;.\;.\; \overset{\delta-}{I} \qquad . \quad . \quad . \quad (B)$$

whilst that for an olefine is a four-point system (C)

$$Br\text{-----}Br\text{-----}CH_2\overset{\text{-----}}{\text{-----}}CH_2 \qquad . \quad . \quad . \quad . \quad (C)$$

in which the two participants may make angular approach to each other. Though the transition complex may eventually yield the $(Br\text{—}CH_2\text{—}CH_2)^+$ cation with the π-bond structure, it is the structure of this critical transition complex (*C*) which will have the higher energy content, and it will be this energy level which is significant in connection with chemical reactivity. Many of the distinctive features of aromatic substitution can be comprehended by considering, in the same way, the energy levels of the critical transition complexes.[38]

Dr. M. J. S. Dewar (*Maidenhead*) (*communicated*) : I have given elsewhere very good evidence that unsaturated hydrocarbons do possess basic properties and can form co-ordination complexes with active acceptors. Dr. Waters' unsupported assertion that π-electrons and unshared *p*-electrons differ qualitatively in their reactions would therefore seem to carry little weight. The essential quantitative differences are that unsaturated hydrocarbons are weaker bases than amines, and that their salts usually undergo secondary reactions immediately.

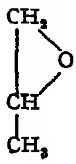
The reactions of olefines with cations do, however, differ qualitatively from their reactions with radicals, for stereochemical evidence shows clearly that in the former case an intermediate with a triangular configuration is formed. Evidence derived from radical reactions is therefore irrelevant in this connection.

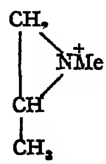
No conclusion can be drawn from the relative reactivities of different reagents with amines and olefines ; there are innumerable cases where reagents show quite different orders of reactivity with different substrates. To give a random example, the $Ph_3C\cdot$ radical reacts more readily with halogen or oxygen than with NO, but with $Ph_2N\cdot$ the reverse is true.

I cannot understand Dr. Waters' statement that " ethylene oxide *cannot* be made by the process of adding an atom of oxygen to ethylene ;

[38] Waters, *J. Chem. Soc.* (in press).

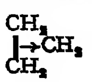
it can only be prepared . . . by treating ethylene chlorohydrin with caustic alkali ". Ethylene oxide is manufactured on a large scale by direct oxidation of ethylene with oxygen over a silver oxide catalyst, a reaction undoubtedly involving simple addition of oxygen atoms to the C=C π-bond; and furthermore, a standard procedure for the preparation of ethylene oxide derivatives is the direct oxidation of the corresponding olefine with perbenzoic or peracetic acids, reactions again involving direct addition of oxygen to the double bond.

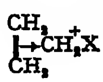

(I)


(II)

The classical structures for ethylene oxide, ethylene imine and cyclopropane do, however, seem to represent their chemical behaviour much better than do the π-complex structures recently proposed by Walsh.[54] Thus in the reactions of propylene oxide (I) and the propylene dimethyliminium[55] ion (II) with bases, the base in each case attacks the *less*-substituted carbon; but when the π-complex intermediates in normal cationoid-addition reactions of olefines react with anions in the second phase of the addition, the anion attacks the *more*-substituted carbon. The former mode of addition would be expected if the compounds were of classical type, the reactions being SN2 replacements in which attack should take place preferentially on the less-alkylated carbon. But the opposite orientation would be expected in a π-complex judging by the calculations reported here. This qualitative difference incidentally provides good evidence that the intermediates in such addition reactions *are* π-complexes.

The chemical unsaturation of cyclopropane can be explained without reference to its electronic structure. The calculations reported here suggest that the unsymmetrical π-complex structure (III) would have a heat of formation comparable with that observed for cyclopropane. Therefore whatever the structure of cyclopropane may be, it should react readily with cations to form genuine π-complexes such as (IV). It is easily shown


(III)


(IV)

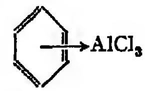
that the most favourable mode of addition by this mechanism to alkylcyclopropane derivatives should be that in which the cation attacks the least-substituted carbon, and the anion attacks the resulting π-complex at the most substituted carbon. Addition to cyclopropane should then obey Markownikoff's rule. This orientation is in fact observed.[56] It is particularly striking that in this case the anion attacks the *more*-alkylated carbon, while with (I) and (II) the reverse is true.

In reply to Mr. Dilke and Dr. Eley,* (1) a moment of 3 D. is too large to be reasonably ascribed to polarisability. There can be very little doubt that the $Et_2O—AlBr_3$ complex is a normal co-ordination compound, and as Mr. Dilke and Dr. Eley themselves point out, its moment agrees closely with that of the $C_6H_6—AlBr_3$ complex; (2) the calculation referred to

[54] Walsh, *Nature*, 1947, 159, 165, 712.
[55] Ross, *J. Amer. Chem. Soc.*, 1947, 69, 2982.
[56] See Davidson and Feldman, *ibid.*, 1944, 66, 488.
* On p. 77.

presumably made use of the observed polarisability of benzene; but this applies to an electric field lying parallel to the ring, and uniform over the ring. The calculated value will then be too large.

Dr. M. J. S. Dewar (*Maidenhead*) said: The very high dipole moment (5 D.) of dilute solutions of aluminium bromide in benzene [57] must imply that co-ordination occurs, a result difficult to explain unless the π-complex (I) is formed. The solubility of $AgClO_4$ in benzene may likewise be due to π-complex formation; other silver salts do not dissolve since they have more covalent character, and hence the Ag^+ in them has lower cationoid activity. The calculations suggest that benzene forms less stable π-complexes than do olefines, and the latter do form complexes with less active silver salts.



(I)

Mr. M. H. Dilke and Dr. D. D. Eley (*Bristol*) (*communicated*): In introducing his paper, Dr. Dewar quoted the dipole moment of 5 D. for the complex $C_6H_6AlBr_3$ as evidence for molecular bond formation involving π electrons. It is also true [58, 59] that for complexes between $AlBr_3$ and various organic substances, including nitrobenzene and diethyl ether, the difference between the moment of the complex and that of the organic molecule is about 5 D.

This appears at first sight to support Dewar's contention of similarity between π bonds and normal semipolar bonds. Closer examination, however, assuming approximate tetrahedral distribution of bonds, shows that about 2 D. can be attributed to the Al—Br bonds, leaving 3 D. for the π bond. A simple calculation indicates that this might easily arise from polarisation of the benzene nucleus by the positively-charged Al atom.

In the field of molecular bond formation it is often necessary to distinguish between bond types. For example, compound formation between $AlCl_3$ and organic molecules might, *a priori*, be due to a co-ordinate link or dipole interaction. Calorimetric measurements [60] in such cases allow an estimate of bond strengths and indicate that they do not depend on the dipole moment of the attached molecule, indicating the former possibility.

Similarly, in the case of a bond such as X—$AlBr_3$, where X is an ethylenic or aromatic hydrocarbon, before postulating π bonds, it is necessary to show that specific changes in bond strength can be observed which may not be explained by a variation in the polarisability of X.

Prof. E. A. Guggenheim (*Reading*) said: Is it right to assert, as implied by Dr. Szwarc, that any molecule containing two unpaired electrons should be paramagnetic? It is certainly obvious that, when every orbital is occupied by two electrons or none, the molecule will be in a singlet state. It is equally obvious that when just one orbital is occupied by only one electron, the molecule will be in a doublet state and so be paramagnetic. If, however, two orbitals each contain only one electron, the molecule can exist in a singlet state and in a triplet state. The question is which of these has the lower energy. We know that for a single atom, such as O, the triplet state has the lower energy. We also know that for a diatomic molecule, such as O_2, the triplet state has the lower energy. Does the triplet state in polyatomic molecules always have lower energy than the singlet? I do not know the answer and ask if there is any theoretical or experimental evidence one way or the other (see p. 320 Weiss)).

Dr. M. Szwarc (*Manchester*) (*communicated*): The problem mentioned by Prof. Guggenheim should be considered separately for two classes of biradicals.

[57] Nespital, *Z. physik. Chem. B.*, 1932, **16**, 153.
[58] Sheka, *J. Physic. Chem., U.S.S.R.*, 1942, **16**, 99.
[59] Nespital, *Z. physik. Chem. B.*, 1932, **16**, 153.
[60] Dilke and Eley (unpublished results).

(*a*) Biradicals in which mere shift of electrons leads to a normal molecule, e.g.  becomes . Every biradical belonging to this class must be paramagnetic (i.e. the electron spins should be parallel). The diamagnetic form (i.e. with paired electron spins) does not represent a separate species, but is a representation of one of the canonical structures among which the "normal" molecule resonates. The magnitude of the contribution of the diamagnetic biradical structure to the ground state of the molecule depends on the separation energy. Probably this separation energy is fairly high, due to the gain of one bond in the "normal" molecular structure.

(*b*) Biradicals which cannot be transferred into the molecular form by electron shifts, i.e. $\cdot CH_2 . CH_2 . CH_2 \cdot$. These radicals can exist in both paramagnetic and diamagnetic forms. The latter form is probably responsible for the production of cyclopropane from trimethylene radicals, as observed by Dr. Bawn.

All the diamagnetic compounds discussed in my paper belong to the former class, and therefore the magnetic criterion is valid and would enable the molecule and the biradical to be distinguished.

Prof. C. A. Coulson (*London*) (*communicated*) : Prof. Guggenheim has asked whether, when a molecule contains two unpaired electrons, the triplet level will necessarily lie lower than the singlet. No completely general proof that the triplet is the lower can be given, although in almost all cases this seems to be true both for atoms and for molecules.

Let the two singly-occupied orbitals be denoted by ϕ and χ. We suppose that the energies E_ϕ and E_χ of the separate orbits are distinct and non-degenerate. Then, if we may presume that the other doubly-occupied orbits are not significantly changed when an electron in ϕ or χ has its spin altered (this condition has been verified for some atoms and is almost certainly satisfied also for molecules), it may be shown that the energy of the singlet exceeds that of the triplet by an amount

$$2\int\frac{\phi(1)\chi(1)\phi(2)\chi(2)}{r_{12}}\,dv_1dv_2.$$

This conclusion is equally true for atoms and for molecules, except for cases like O_2, where $E_\phi = E_\chi$, and like benzene, where both ϕ and χ are degenerate, so that excitation gives rise to more than one singlet and one triplet. Such cases must be dealt with on their merits.

The important contributions to the integral above occur where the products $\phi(1)\chi(1)$ and $\phi(2)\chi(2)$ are both large and r_{12} is small. That means that the electrons are close together, so that $\phi(1)\chi(1)$ and $\phi(2)\chi(2)$ will have the same sign. We should therefore expect that the integral would be positive, and the singlet would be higher than the triplet.

If one uses the method of molecular orbitals for conjugated molecules, then for the lowest excited state (which is the one responsible for colour, etc.) ϕ and χ are simply related to each other (energies $= E_0 \pm k\beta$, in the usual notation). It may then be shown that the integral is necessarily positive, making the triplet state lowest. But this argument does not apply to more excited levels, in some of which it may break down.

So far as experimental evidence is concerned, the recent work of Lewis, Kasha and others in America has shown that for the first excited levels of a large number of condensed hydrocarbons and hetero-systems, without exception the triplet lies considerably lower than the singlet. On the energy scale, the triplet comes between one-half and one-third of the distance from the singlet to the ground level.

II.—GAS PHASE.

A.—HYDROCARBON RADICALS.

INTRODUCTORY REMARKS

Prof. C. N. Hinshelwood (*Oxford*) said: In his theoretical introduction Prof. Coulson comments on the limited nature of our knowledge of alkyl radicals. It seems to be one of the disappointments of modern theories that they so seldom give us indications of new qualitative principles, but on the whole serve as methods for quantitative interpolation and extrapolation. However this may be, it looks as though we shall depend for some time upon experimental observations to initiate fresh advances.

From the group of papers before us there emerges a number of properties of free radicals, or at least a number of interesting questions about such properties.

Dyne and Style point out the rarity of band spectra due to polyatomic radicals and cite CHO, NH_2 and CH_2 as among the few known examples. They obtain HCO in the fluorescence of formaldehyde and identify it with the corresponding band in hydrocarbon flames. Gaydon and Wolfhard show that HCO occurs in flames at an early stage of the combustion process. Coleman and Gaydon confirm the attribution of certain bands to BrO and discuss bands thought to be due to CBr.

A theoretical question arises from the comparative rarity of the polyatomic radical band. In a system A—B—, is there a special tendency to split to A— +B, if B is a possible saturated molecule ?

The radical HO_2 is important in that quite a lot of interesting chemistry would have to be rewritten if we were not allowed to postulate its existence. Minkoff accepts the indirect evidence, adds some more from experiments of Egerton and Minkoff on hydrogen peroxide and shows that the existence of HO_2 is supported by the well-known " semi-empirical " method. It is a pity that the strictures passed upon the quantitative side of this method at the Manchester Meeting of the Faraday Society in 1937 still have some force.

The next set of problems relates to the behaviour of radicals when they meet one another or other molecules.

(*a*) When they meet one another disproportionation, according to Bawn and Tipper (who generate them from a halide and *excess* of sodium), seems to prevail over dimerisation. One can see a possible theoretical treatment of this and it would be interesting to develop it.

(*b*) When radicals meet unsaturated molecules the collision efficiency is perhaps lower than one might expect. Robb and Melville find about 10^{-4} for hydrogen atoms and propylene (by a method in which rate of hydrogenation is made to compete with the hydrogen atom—MoO_3 reaction).

(*c*) Steacie, Darwent and Trost in a tentative assignment of steric factors for reactions of radicals with hydrocarbons arrive at a gradation from 10^{-1} for $H + H_2$, to 10^{-4} for CH_3 + *iso*butane.

(*d*) As to the inherent stability of radicals an interesting question arises about methylene. Norrish and Porter challenge the idea that CH_2 has a life long enough to justify the name " molecule," find that its life in ketene is only of the same order as that of CH_3 in acetone and regard it as existing in the bi-radical state. Bawn and Tipper on the other hand claim that certain chemiluminescent effects can only be explained if the re-organisation energy of CH_2 is emitted on formation.

In an attempt to correlate the major qualitative facts of hydrocarbon oxidation and pyrolysis, Cullis, Hinshelwood, Mulcahy and Partington attribute importance (*a*) to the tendency of radicals RCH_2O— to split into R— +HCHO and (*b*) to the influence of the structure of R on the tendency of the peroxide R—O—O—R to split into radicals of the form R—O—. Quite apart from any relevance to hydrocarbon combustion the theoretical consideration of (*a*) and (*b*) would be extremely interesting.

ELEMENTARY REACTIONS INVOLVING THE LOWER PARAFFINS.*

By E. W. R. Steacie, D. de B. Darwent and W. R. Trost.

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Elementary reactions of atoms and radicals have become of major importance in the interpretation of chemical mechanisms. Among the most important of such reactions are those of the types :

$$H + RH \rightarrow H_2 + R \quad . \quad . \quad . \quad . \quad (1)$$

and

$$CH_3 + RH \rightarrow CH_4 + R, \quad . \quad . \quad . \quad (2)$$

where RH is a paraffin hydrocarbon. A great deal of work has been done on these reactions, but there are considerable discrepancies in the data.[1]

In work of this kind one of two procedures is usually, of necessity, adopted.

(*a*) The appearance of a final product is determined as a function of temperature. From this the activation energy of an elementary reaction is calculated. In the absence of a knowledge of the absolute rate of the reaction, the steric factor cannot be determined, and is usually arbitrarily put equal to 0·1. Reactions of type (2) are examples.

(*b*) The collision yield is determined at room temperature only, and on the assumption that the steric factor s is 0·1 an activation energy is calculated.

With inc easing knowledge of the rates of such reactions, it is important thatrmore consideration be given to the steric factors. In the present paper the data are reviewed from this point of view, and it is concluded that conflicting data can be reconciled by means of suitable assumptions about the steric factors.

I. Reactions of the Type : $H + RH \rightarrow H_2 + R$.

In view of the fact that a detailed discussion of these reactions has recently been given,[1] we will merely refer to the "best" present values of the data.

$$H + CH_4 \rightarrow CH_3 + H_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The results of various workers lead to $E_3 = 12·9 \pm 2$ kcal. (assuming $s = 0·1$), or 10·9 kcal. ($s = 0·01$). This is one of the few H-atom reactions where the activation energy calculated from the temperature coefficient is in reasonable agreement with collision-yield data.

$$H + C_2H_6 \rightarrow C_2H_5 + H_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A recent recalculation of the data[4] at room temperature leads to the following values of E_4.

Trenner, Morikawa and Taylor[2]	8·5 kcal.	($s = 0·1$)
Steacie[3]	8·8 ,,	($s = 0·1$)
Trost and Steacie[4]	9·0 ,,	($s = 0·1$)

* Contribution No. 1558 from the National Research Council, Ottawa, Canada.

[1] See, for example, Steacie, *Atomic and Free Radical Reactions* (New York, 1946).

[2] Trenner, Morikawa and Taylor, *J. Chem. Physics*, 1937, 5, 203.

[3] Steacie, *J. Chem. Physics*, 1938, 6, 37.

[4] Trost and Steacie (unpublished).

$H + C_3H_8 \rightarrow C_3H_7 + H_2$ . . . . (5)

Trost's recent value of E_5,[4] in good agreement with previous workers' is 8·7 ± 0·4 kcal. (s = 0·1).

$H + n\text{-}C_4H_{10} \rightarrow C_4H_9 + H_2$. . . . . (6)

The results of Steacie and Brown [5] led to $E_6 = 9 \pm 1{\cdot}5$ kcal. (s = 0·1). Errors in the atom concentrations in this work have been pointed out,[6] and a correction and comparison with *iso*-butane gives $E_6 = 9{\cdot}3$ kcal. (s = 0·1).

$H + iso\text{-}C_4H_{10} \rightarrow C_4H_9 + H_2$. . . . . (7)

White, Winkler and Kenalty [6] found a value of E_7 of 9·3 kcal. (s = 0·1) from collision-yield data at room temperature.

$H + neo\text{-}C_5H_{12} \rightarrow C_5H_{11} + H_2$. . . . . (8)

Recent work of Trost [4] leads to $E_8 = 9{\cdot}2$ kcal. (s = 0·1). We thus arrive at the values given in Table I.

TABLE I.

Compound RH.	Activation Energy of $H + RH \rightarrow H_2 + R$, Calculated from Collision Yield at Room Temperature, Assuming s = 0·1.	Activation Energy of $CH_3 + RH \rightarrow CH_4 + R$ Calculated from Temperature Coefficient of CH_4 Production.
H_2	—	8·1
CH_4	12·9	—
C_2H_6	9·0	8·3
C_3H_8	8·7	—
$n\text{-}C_4H_{10}$	9·3	5·5
$iso\text{-}C_4H_{10}$	9·3	4·2
$neo\text{-}C_5H_{12}$	9·2	8·3

From these data the activation energy of the reaction of H atoms with methane appears to be higher than the corresponding values for the other simple paraffins, all of which are about the same. The values listed in Table I are peculiar, however, for several reasons.

(*a*) The drop in activation energy on going from methane to ethane is to be expected on account of the lower C—H bond strength. The indications are, however, that there is a steady decrease in bond strength from CH_4 to C_4H_{10}. Thus from the results of Polanyi *et al.* we have: [7]

CH_3—H	102·5 kcal.
C_2H_5—H	97·5 ,,
$n\text{-}C_3H_7$—H	95·0 ,,
$n\text{-}C_4H_9$—H	94·0 ,,
$iso\text{-}C_3H_7$—H	89·0 ,,

Hence the activation energies of the H-atom reactions would have been expected to diminish as we go up the series.

(*b*) A still more sharp diminution in activation energy would have been expected on going from ethane to propane, since propane contains secondary hydrogens, and these are more weakly bound. On the basis of Polanyi's data the $iso\text{-}C_3H_7$—H bond is 8·5 kcal. weaker than the C_2H_5—H bond. Furthermore, there is direct experimental evidence that

[5] Steacie and Brown, *J. Chem. Physics*, 1940, 8, 734.
[6] White, Winkler and Kenalty, *Can. J. Res. B*, 1942, 20, 255.
[7] See [1] for references.

in the reaction of hydrogen atoms with propane, secondary hydrogens *are* removed.[8]

A similar decrease would have been expected with *iso*-butane, since tertiary hydrogen atoms are still more weakly bound.

(*c*) The activation energies of the reactions

$$CH_3 + RH \rightarrow CH_4 + R$$

would be expected to run roughly parallel to those of

$$H + RH \rightarrow H_2 + R.$$

The last column of Table I shows that the expected decrease in activation energy for the removal of secondary and tertiary H atoms by methyl radicals does occur, although its magnitude is less than would have been expected from bond-strength values. There is thus little or no similarity between the activation energies for the two types of reaction.

The Temperature Coefficients of Hydrogen-Atom Reactions.

The activation energies listed in the second column of Table I are derived from collision-yield data at room temperature, on the assumption that the steric factor is 0·1. In the investigation of atomic reactions by the discharge tube method not much weight is usually given to temperature coefficients, since the atom concentrations at the different temperatures are usually rather uncertain. This uncertainty causes a relatively small error in activation energies calculated from collision yields, since an error of a factor of 2 in the collision yield at room temperature will only cause an error of 0·4 kcal. in the calculated activation energy. In view of the small temperature coefficients of the reactions, however, such an error in the atom concentrations makes the activation energies calculated from the collision yields very unreliable.

It has, however, been noted for a considerable time that the temperature coefficients of the reactions of H atoms with the paraffins were much smaller than those calculated from collision yields, assuming $s = 0{\cdot}1$. (Or, put in another way, the activation energies calculated from collision yields at high temperatures were higher than those calculated from collision yields at low temperatures.) The reaction of hydrogen atoms with methane is a conspicuous exception, since in this case the activation energy calculated from the temperature coefficient is in excellent agreement with that from collision yields. There appear to be two possible explanations. (1) The steric factors in these reactions are much smaller than 0·1; (2) the H-atom concentrations at high temperatures are much smaller than those assumed. As an example we may consider the case of propane.[9] The average values of the activation energy calculated from the collision yield (assuming $s = 0{\cdot}1$) are 8·8 kcal. at 32° C. and 13·0 kcal. at 250° C. The ratio of the average collision yield at 250° C. to that at 32° C. is

$$3{\cdot}83 \times 10^{-7}/4{\cdot}97 \times 10^{-8} = 7{\cdot}7.$$

Actually, for an activation energy of 8·8 kcal. the ratio should be approximately 400. The experimental ratio corresponds to an activation energy of 3·0 kcal. The value calculated from a smoothed log (collision yield) $- 1/T$ plot is about 4 kcal.

The results for other substances are similar, thus the ratios of the collision yields at 250° and 30° C. are approximately 13·5 for *n*-butane and 8 for *iso*-butane, again corresponding to activation energies less than 4

[8] Steacie and Dewar, *J. Chem. Physics*, 1940, 8, 571.

[9] Steacie and Parlee, *Trans. Faraday Soc.*, 1939, 35, 854; *Can. J. Res. B*, 1939, 17, 371.

kcal. The results therefore suggest that the activation energies of these reactions are lower than has previously been assumed, with correspondingly low steric factors.

The low temperature coefficients, however, may be in part (or possibly wholly) due to the H-atom concentrations at high temperatures being much lower than the assumed values on account of the rapid consumption by reaction of H-atoms at the higher temperatures, and the fact that atom concentrations are measured in blank runs.

It is therefore of interest to calculate how many H atoms are used relative to those available in runs at higher temperatures with different substances. The values obtained for the 3 best-investigated substances are given in Table II.

In the case of methane, if we assume the mechanism

$$H + CH_4 \rightarrow CH_3 + H_2$$
$$CH_3 + H(+ M) \rightarrow CH_4(+ M),$$

2 H atoms are consumed for each molecule of CH_4 reacting, or less if the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

is of importance. There are 4·4 available at 500° c., and hence only about

TABLE II.

Hydrocarbon, *RH*.	Temp., °*c*.	H-atoms available per Molecule of RH Reacting.	Maximum number of H-atoms Consumed per Molecule of RH Reacting.
CH_4	500	4·4	2
C_3H_8	32	17·4	6
	250	5·9	6
iso-C_4H_{10}	250	9·3	8

half the atoms are consumed even at the highest temperature. This will not make an appreciable error, and it is significant that in this case the temperature coefficient is approximately what would be expected from the collision yield. This is a favourable case, however, since the activation energy is high and the percentage reaction is therefore small, and also at most 2 H atoms are consumed per molecule reacting.

In the case of propane and of *iso*-butane the values in the last column are again calculated neglecting atom-reforming reactions, and are therefore maximum values. Nevertheless, it is evident that there is a definite possibility of the high temperature collision yields being too low on account of the diminished H-atom concentration. It seems likely, however, that while some error is involved from this cause, the collision yield activation energies are also too high because of the assumption of insufficiently low steric factors.

In view of the possible errors in H-atom concentrations, and of the fact that all investigations were made under very similar conditions it is of interest to compare the actual percentage reaction at room temperature for different hydrocarbons, as determined by various workers. If this is done it is found that the maximum variation in reactivity at room temperature for all paraffins other than methane is only by a factor of about 10. It follows that if there are any considerable differences in the activation energies of the reactions, they must be largely offset by corresponding differences in the steric factor.

II.—Reactions of the Type : $CH_3 + RH \rightarrow CH_4 + R$.

$CH_3 + H_2 \rightarrow CH_4 + H$.

This reaction has been investigated by a number of workers [10–14] who are in general agreement in assigning it an activation energy of approximately 8 kcal. The investigation of Cunningham and Taylor is the most reliable and leads to an activation energy from the temperature coefficient,, of 6·6 to 8·1 kcal. with the higher limit tho more likely. Patat [11] concluded from his results on the ortho-para hydrogen conversion in the presence of photolysing acetaldehyde that the activation energy was 9 kcal., *with a steric factor of* 10^{-4}. He argues quite reasonably that a value of 8 or 9 kcal. must be combined with a small steric factor, since otherwise in the Paneth technique with hydrogen as a carrier it would be impossible for radicals to emerge from the hot furnace without reacting with hydrogen.[15] While too much liance cannot be placed on the exact value of s which he obtains, it seems to be fairly well established that the steric factor is low for this reaction.

$$CH_3 + RH \rightarrow CH_4 + R.$$

Smith and Taylor [16] investigated the photolysis of mixtures of mercury dimethyl with a number of paraffin hydrocarbons. The main facts from their work are :

(*a*) the formation of ethane in the absence or presence of hydrogen remains unchanged;

(*b*) the formation of methane increases rapidly with temperature, and this increase is paralleled by an increase in the rate of decomposition of mercury dimethyl;

(*c*) the rate of mercury dimethyl decomposition is independent of concentration ;

(*d*) hydrocarbons produce the same general effects as added hydrogen.

They propose the following mechanism :

$$\begin{array}{lr} Hg(CH_3)_2 + h\nu \rightarrow 2CH_3 + Hg & I_{abs.} \\ CH_3 + RH \rightarrow CH_4 + R & k_1 \\ R + CH_3 \rightarrow RCH_3 & k_2 \\ CH_3 + CH_3 \rightarrow C_2H_6 & k_3 \end{array}$$

The reaction

$$CH_3 + Hg(CH_3)_2 \rightarrow C_2H_6 + CH_3 + Hg$$

is also postulated, but is ignored in the mechanism since it produces one CH_3 for each CH_3 consumed, and does not affect methane production.

The mechanism is perhaps over-simplified, but it is very difficult to improve on it, and it appears to be well established as far as methane production is concerned.

For the rate of methane production the mechanism leads to *

$$\frac{d}{dt}(CH_4) = \frac{k_1}{2k_3}(RH)\left\{-2k_1(RH) + (4k_1^2(RH)^2 + 8k_3I_{abs.})^{1/2}\right\}$$

Smith and Taylor assume that the term in large brackets is constant, and hence

$$\frac{d}{dt}(CH_4) = \text{const. } k_1 \text{ (RH)}.$$

[10] Hartel and Polanyi, *Z. physik. Chem. B*, 1930, **11**, 97.
[11] Patat and Sachsse, *ibid.*, 1935, **31**, 105. Patat, *ibid.*, 1936, **32**, 274.
[12] Spence and Wild, *Proc. Leeds Phil. Soc.*, 1936, **3**, 141.
[13] Taylor and Rosenblum, *J. Chem. Physics*, 1938, **6**, 119.
[14] Cunningham and Taylor, *ibid.*, 1938, **6**, 359.
[15] See Rice, *J. Amer. Chem Soc.*, 1934, **56**, 488.
[16] Smith and Taylor, *J. Chem. Physics*, 1939, **7**, 390.
* In the paper of Smith and Taylor there is a misprint and the second term in the bracket is given as $4k_1(RH)^2$ instead of $4k_1^2(RH)^2$.

Hence the activation energy measured is that of reaction (1). In this way, they get for the activation energies of the reactions

$$CH_3 + RH \rightarrow CH_4 + R$$

the values given in column 3 of Table I. Smith and Taylor have suggested that the differences in activation energies in the above results are to be explained on the basis of a diminution in the strength of the C—H bond in secondary and tertiary positions, and that the observed differences in activation energy are to be equated directly to the differences in bond strengths. The differences, however, are much smaller than the bond strength differences estimated by Polanyi.[7]

The main doubtful point in the above derivation is the assumption that

$$A = \frac{-2k_1(RH) + (4k_1^2(RH)^2 + 8k_3I_{abs.})^{1/2}}{2k_3}$$

is approximately temperature-independent. The condition for this is that

$$8k_3I_{abs.} \gg 4k_1^2(RH)^2.$$

Under these circumstances A reduces to

$$A = \frac{(8k_3I_{abs.})^{1/2}}{2k_3},$$

and since E_3 is small, A will be virtually independent of temperature. On the other hand if

$$8k_3I_{abs.} \ll 4k_1^2(RH)^2,$$

the rate equation becomes

$$\frac{d}{dt}(CH_4) = I_{abs.},$$

i.e. methane production is independent of temperature, is the same for all hydrocarbons, and no appreciable amount of ethane is produced. This is certainly not the case.

It is therefore of interest to make a rough estimate of the magnitudes of the two terms. In the middle of the temperature range employed we have: $T = 700°$ K.; $I_{abs.} = 10^{-5}$ einstein/litre (this is not stated, but must be roughly correct); $(RH) = 200$ mm. $= 4{\cdot}5 \times 10^{-3}$ mole/litre. If we assume bimolecular rate constants to be given approximately by

$$k = 10^{10}s\, e^{-E/RT}, \text{ then}$$

or $E_3 = 0, \quad s_3 = 1,\ k_3 = 10^{10};$

for $E_1 = 9$ kcal., $s_1 = 1,\ k_1 = 1{\cdot}6 \times 10^7.$

Hence

$$8k_3I_{abs.} = 8 \times 10^5$$
$$4k_1^2(RH)^2 = 2 \times 10^{10}$$

i.e. $$8k_3I_{abs.} \ll 4k_1^2(RH)^2.$$

If $s_1 \ll s_3$ it would be possible to reverse this, but it seems most unlikely that a metathesis should have a much smaller steric factor than a recombination reaction. However, since k_3 appears to the first power and k_1 to the second, if both steric factors are small $8k_3I_{abs.}$ can be made greater than $4k_1^2(RH)^2$. To do this will require roughly

$$s_1 = s_3 = 10^{-5}.$$

For lower values of E_1, such as 5·5 kcal. for C_3H_8, the difference is still greater, and it will require values of s_1 of the order of 10^{-7} to make the term A temperature-independent.

It follows that Taylor and Smith's calculations of the activation energies of methyl-hydrocarbon reactions are not valid unless very small steric factors are assumed for reactions of the type

$$CH_3 + RH \rightarrow CH_4 + R.$$

Their results are, however, very consistent, and give excellent log (CH_4 production) $- 1/T$ plots at higher temperatures. The data may therefore be considered as offering strong support for low steric factors in these reactions.

TABLE III.

Reaction.	$k_{CH_4} \times 10^3$ at 562° K., in Arbitrary Units.
CH_3+H_2	120*
C_2H_6	35·2
n-C_4H_{10}	59·6
iso-C_4H_{10}	56·3
neo-C_5H_{12}	60·5

It is possible also to get an indication of the relative values of the steric factor for different hydrocarbons from Smith and Taylor's work. The absolute values of k_{CH_4}, the rate of methane production, from their results at a fixed temperature are given in Table III.

It will be noted that the values do not show the spread to be expected from the activation energy differences. It follows that the variations in activation energy are being compensated by variations in the steric factor, and to bring the results into line requires

$$s_{\text{primary}} : s_{\text{secondary}} : s_{\text{tertiary}} \sim 1 : 0{\cdot}1 : 0{\cdot}03.$$

Hence if we put

$$s_{\text{primary}} = s_{H_2} = 10^{-4},$$

we obtain the values

$$s_{\text{primary}} = 10^{-4} \quad (C_2H_6 \text{ and } neo\text{-}C_5H_{12})$$
$$s_{\text{secondary}} = 10^{-5} \quad (C_3H_8 \text{ and } n\text{-}C_4H_{10})$$
$$s_{\text{tertiary}} = 10^{-6} \quad (iso\text{-}C_4H_{10}).$$

These values seem reasonable, and are of the same order as those required to justify the kinetic treatment of Smith and Taylor.

III. Comparison of H-Atom and Methyl-Radical Reactions.

In a reaction such as

$$H + CH_4 \rightleftharpoons CH_3 + H_2$$

the difference between the steric factors of the forward and reverse reactions will be governed by the magnitude of the entropy change in the reaction, and would not be expected to be very great. The absolute magnitude of the steric factor will be governed for each reaction by ΔS^*, the difference in entropy between the initial and the transition state. If ΔS^* is negative the steric factor will be small.

According to Eyring [17] ΔS^* will be negative for a reaction between polyatomic molecules, and moderate for a reaction between an atom and a polyatomic molecule. It is to be expected, therefore, that a reaction of the type

$$CH_3 + C_4H_{10} \rightarrow CH_4 + C_4H_9$$

should have a very small steric factor,[18] and it does not seem unreasonable also that a reaction of the type

$$H + C_4H_{10} \rightarrow H_2 + C_4H_9$$

should have a fairly small steric factor. Furthermore, it would be expected that the steric factors and activation energies of methyl-radical and H-atom reactions with paraffins would vary with the molecular configuration in a roughly parallel way.

On the basis of these considerations, and of the evidence for low steric factors in these reactions discussed previously, the following table is

* Extrapolated from the value at 539° K.

[17] Glasstone, Laidler and Eyring, *The Theory of Rate Processes* (New York, 1941), p. 19.

[18] See also Moore and Taylor, *J. Chem. Physics*, 1940, 8, 396.

presented as an attempt to make the most plausible assignment of activation energies and steric factors.

It should be emphasised that while these values are to some extent a mere guess, there does appear to be very definite evidence that the steric

TABLE IV.

Reaction.	E, kcal.		S.	
	X = H.	X = CH_3.	X = H.	X = CH_3.
X + H_2	6·2	8·1	10^{-1}	10^{-1}
CH_4	10·9	—	10^{-3}	—
C_2H_6	8·3	8·3	10^{-2}	10^{-4}
C_3H_8	5·5	5·5	10^{-4}	10^{-5}
n-C_4H_{10}	5·5	5·5	10^{-4}	10^{-5}
iso-C_4H_{10}	4·2	4·2	10^{-5}	10^{-6}

factors in these reactions are all very low. It is hoped that further work on H-atom reactions at high temperatures may give a direct answer to the question. In the meantime, Table IV represents merely our opinion of the most likely values based on present available data.

Summary.

A discussion is given of published data on the rates of reactions of the types :

$$H + RH \rightarrow R + H_2$$

and

$$CH_3 + RH \rightarrow R + CH_4,$$

together with some new results. The existing data show many inconsistencies, the causes of which are discussed. It is concluded that the various results can only be reconciled on the assumption of much lower steric factors for certain reactions than have previously been assumed.

Résumé.

On donne une discussion de résultats déjà publiés—ainsi que quelques nouveaux—sur les vitesses des réactions suivantes :

$$H + RH \rightarrow R + H_2$$
$$CH_3 + RH \rightarrow R + CH_4.$$

Les données existantes présentent de nombreuses contradictions, dont on fait la critique. On conclut que les divers résultats peuvent s'accorder si l'on suppose pour certaines réactions, des facteurs stériques très inférieurs à ceux attribués précédemment.

Zusammenfassung.

Veröffentlichte und einige neue Daten über die Geschwindigkeiten von Reaktionen der Typen

$$H + RH \rightarrow R + H_2$$

und

$$CH_3 + RH \rightarrow R + CH_4$$

und Widersprüche in diesen Daten werden erörtert. Es wird gefolgert, dass die Daten nur bei Annahme von sterischen Faktoren, die weit kleiner als bisher vorgeschlagene sind, vereinbar sind.

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RELATIVE REACTIONS RATES OF CHLORINE ATOMS WITH PRIMARY, SECONDARY AND TERTIARY HYDROGEN ATOMS IN HYDROCARBONS.

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It has long been known that the activation energy of a given reaction is closely related to the bond strength of the bonds to be formed or to be broken. This applies particularly to substitution reactions of the type:

$$A + BR \rightarrow AB + R.$$

A relevant example is found in the reactions of organic halides with sodium vapour studied by Polanyi and co-workers.[1]

More recently significant differences, both in bond strength and in activation energy, were discovered in reactions of organic molecules, depending on whether primary, secondary or tertiary carbon bonds were involved. Thus, Smith and Taylor [2] in an investigation of the reactions of methyl radicals with various hydrocarbons, reactions of the type:

$$CH_3 + HR \rightarrow CH_4 + R,$$

where R is an alkyl residue, observed that the activation energy of the reaction varies with the number of hydrogen atoms on the carbon atom at which the substitution takes place. For ethane and *neo*pentane, i.e., for reaction at a primary carbon atom, the values of the activation energies were found to be 8·3 kcal. per mole in either case. In the case of butane the value found was 5·5 kcal. per mole, while for *iso*butane it was 4·2 kcal. per mole.

The authors conclude that since the activation energies for the reactions with ethane and *neo*pentane are the same, the removal of a hydrogen atom from a primary carbon atom is energetically independent of the nature of the hydrocarbon.

On the basis of these results, together with results quoted from other workers,[3] Smith and Taylor suggested that the bond energy of a C—H bond be reduced by 2·5 kcal. per mole for a secondary carbon atom, and 4 kcal. per mole for a tertiary atom below the value of the energy of the C—H bond for the corresponding primary carbon atom. Clearly this recommendation is based upon the assumption of an equality between variation of bond strength and variation of the activation energy of a reaction involving splitting of the bond.

Owing largely to the recent work of Polanyi and co-workers we now have a much clearer understanding, in some cases at least, of the relation between bond strength and activation energy in reactions involving organic molecules. In the first place it is now clear that there is a decrease in bond strength in passing from a primary C—H bond to a secondary, and a still further decrease for a tertiary bond. Further, the energy of a particular bond, for instance a primary bond, is dependent on the number of carbon atoms in the molecule. A part of the revised table of bond energies, after Polanyi,[1] is quoted here in illustration of these facts and as being relevant to the present work.

[1] Butler and Polanyi, *Trans. Faraday Soc.*, 1943, 39, 19.
[2] Smith and Taylor, *J. Chem. Physics*, 1939, 7, 390.
[3] Kistiakowsky, Ruhoff, Smith and Vaughan, *J. Amer. Chem. Soc.*, 1936, 58, 137.

Secondly, of importance in the present connection, Polanyi finds that for a certain class of reactions, namely the reactions of alkyl halides with sodium atoms:

$$Na + ClR \rightarrow NaCl + R,$$

there exists a proportionality

$$\Delta E = \alpha \Delta Q,$$

where ΔQ is the change in bond energy (more strictly the change in heat of reaction) in passing from one alkyl group R to another, and ΔE is the corresponding change in the activation energy of the reaction quoted. The value of α is shown theoretically[4] to lie between zero and unity: the experimental value is 0·27.

TABLE I.

BOND ENERGIES OF C—H BONDS, AFTER POLANYI.

R.	$Q_{R—H}$, kcal. per mole.
CH_3	102·5
C_2H_5	97·5
n-C_3H_7	95·0
n-C_4H_9	94·0
iso-C_3H_7	89·0
$tert$-C_4H_9	86·0

It is the purpose of the present paper to show that similar conditions obtain in substitution reactions of chlorine atoms and hydrocarbons, as will be shown in the following paragraphs.

Substitutive Chlorination Reactions.

The substitutive chlorination of hydrocarbons takes place according to the overall reaction:

$$RH + Cl_2 \rightarrow RCl + HCl$$

but it is now generally accepted that such reactions proceed by a mechanism involving reaction chains initiated by chlorine atoms:

$$Cl + RH = R + HCl$$
$$R + Cl_2 = RCl + Cl.$$

This mechanism cannot be said to have been established beyond all doubt. However, the evidence in its favour is very considerable.[5] In any case, any doubts which might be cast upon it relate rather to the chain-termination steps rather than to the actual chain propagation. Such uncertainties, however, do not affect the present issue. The alternative mechanism:

$$Cl + RH \rightarrow RCl + H;$$
$$Cl_2 + H \rightarrow HCl + Cl,$$

may be discounted as being energetically unfavourable.

The reaction takes place at relatively low temperatures, above about 200° C. At that temperature the thermal equilibrium dissociation of Cl_2 into chlorine atoms, and equally the homogeneous rate of dissociation, is very small and cannot account for the observed rate of reaction. On the other hand, no substantial influence of the surface in increasing the rate of the reaction has been noted.[5] From these facts we conclude that the reaction chains both start and conclude on the wall. Thus the reaction takes place according to the following mechanism:

$$\begin{array}{ll} Cl_2 + \text{wall} \rightarrow 2Cl & d \\ Cl + RH \rightarrow HCl + R & k_1 \\ R + Cl_2 \rightarrow RCl + Cl & k_2 \\ Cl + \text{wall} \rightarrow \text{adsorbed Cl} & r \end{array}$$

Using the usual stationary-state treatment this leads to the following equation for the formation of RCl:

$$\frac{d(RCl)}{dt} = k_1 \cdot \frac{d}{2r} \cdot (RH) \cdot (Cl_2) \quad . \quad . \quad . \quad (1)$$

[4] Evans and Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11.

[5] Pease and Walz, *J. Amer. Chem. Soc.*, 1931, **53**, 3728; Yuster and Reyerson, *J. Chem. Physics*, 1935, **39**, 859; Vaughan and Rust, *J. Org. Chem.*, 1940, **5**, 449.

which shows that apart from the constants governing the formation and recombination of chlorine atoms the rate of substitution is governed by that of reaction (k_1) only.

While formula (1) does not allow one to calculate the rate of reaction (k_1) because nothing is known of the dissociation and recombination rates (d) and (r), it nevertheless affords a convenient means of comparing relative substitution rates, for instance on primary and secondary carbon atoms of the same hydrocarbon molecule. Assuming the substitution reaction to be carried out on propane, we find for substitution on the primary carbon atoms, leading to 1-chloropropane:

$$\frac{d(R_1Cl)}{dt} = k_1^{I} \cdot \frac{d}{2r} \cdot (RH) \cdot (Cl_2) \qquad (2)$$

and for substitution on the secondary atoms leading to 2-chloropropane:

$$\frac{d(R_2Cl)}{dt} = k_1^{II} \cdot \frac{d}{2r} \cdot (RH) \cdot (Cl_2) \qquad (3)$$

Dividing (2) by (3) we find:

$$\frac{d(R_1Cl)}{d(R_2Cl)} = \frac{k_1^{I}}{k_1^{II}}$$

or, integrated:

$$\frac{(R_1Cl)}{(R_2Cl)} = \frac{k_1^{I}}{k_1^{II}} \qquad (4)$$

This shows that the relative yields of the primary- and secondary-reaction products directly give the ratio of the two rates. Thus from a quantitative examination of the products of substitution reactions the relative rates of the reaction of a chlorine atom with a hydrogen atom bound to a primary or secondary carbon atom can be calculated. Such experiments were carried out by Hass and collaborators.[8]

Hass has measured the relative amounts of primary, secondary, and tertiary monochlorides produced by substitutive chlorination, in hydrocarbons from which at least two isomeric products can be formed. The reactions with propane and *iso*butane were investigated at a series of temperatures, and various ratios of hydrocarbon to chlorine in the reaction mixture; also four other hydrocarbons, viz., butane, pentene, *iso*-pentane and pentane were used, each at one temperature and one hydrocarbon/chlorine ratio. That part of Hass' data relative to the present discussion is presented in Table II.

The results in Table II give no information from which absolute rate constants may be found, but, as explained above and as shown below, from the relative amounts of the substitution products, the ratios of rate constants for reaction at different carbon atoms may be calculated. Hass defines a "relative selection" (R.S.), which takes into account the *a priori* probabilities of substitution at the various kinds of carbon atom, these being dependent on the number of hydrogen atoms which are available for substitution on each carbon atom. Thus, where n_2 is the number of hydrogen atoms on a secondary carbon atom, n_1 the number on a primary carbon atom, and $(R.S.)_{2°,1°}$ the relative selection in favour of secondary substitution, we have:

$$(R.S.)_{2°,1°} = \frac{\%\ 2°\ \text{product}}{\%\ 1°\ \text{product}} \cdot \frac{n_1}{n_2} \qquad (5)$$

An analogous relation holds for tertiary substitution.

Clearly the relative selection defined in the above manner is equivalent

[8] Hass, McBee and Weber, *Ind. Eng. Chem.*, 1936, 28, 333.

to the ratio of the rate constants for the corresponding substitution reactions (see eqn. (4)). Then, where k is the rate constant, E the activation energy, and A the temperature-independent term in the Arrhenius equation, we have :

$$\log_{10} (\text{R.S.})_{2°,1°} = \log_{10}\frac{A_2}{A_1} + \frac{1}{T}\cdot\frac{E_1 - E_2}{2{\cdot}303R} \quad . \quad . \quad (6)$$

$$\log_{10} (\text{R.S.})_{3°,1°} = \log_{10}\frac{A_3}{A_1} + \frac{1}{T}\cdot\frac{E_1 - E_3}{2{\cdot}303R} \quad . \quad . \quad (7)$$

The subscripts 1, 2, 3 in these equations refer to primary, secondary and tertiary substitution respectively.

TABLE II.—RELATIVE SUBSTITUTION AT PRIMARY, SECONDARY AND TERTIARY CARBON ATOMS IN THE MONOCHLORINATION OF HYDROCARBONS, AFTER HASS.[6]

Hydrocarbon.	Temp. °C.	Ratio Hy/Cl.	% 1°.	% 2°.	% 3°.
Propane . .	490	2	55·7	44·3	—
,, . .	300	2	47·6	52·4	—
,, . .	600	9	57·8	42·2	—
,, . .	475	21	53·9	46·1	—
,, . .	550	16	58·4	41·6	—
,, . .	300	8	47·2	52·8	—
*Iso*butane . .	400	2	70·8	—	29·2
,, . .	325	2	68·8	—	31·2
,, . .	375	2	69·1	—	30·9
,, . .	400	8	70·2	—	29·8
,, . .	600	2	76·5	—	23·5
,, . .	300	2	66·5	—	33·5
,, . .	300*	2	66·7	—	33·3
Butane . .	300	7	32·0	68·0	—
Pentene . .	330	16	24·0	76·0	—
*Iso*pentane . .	330	16	50·0	28·0	22·0
Pentane . .	440	7·5	30·0	70·0	—

In cases where the temperature dependence of the relative selection is known, the ratio of the A-factors and the difference of the activation energies may be found, though neither of these values may be found absolutely by this method. The necessary data are available only in the cases of substitution of propane and *iso*butane. In Table III are shown the results of calculations from these data, and, in Fig. 1, the logarithm of the relative selection is plotted against the reciprocal of the absolute temperature for these two hydrocarbons.

In either case, a reasonably straight line passing through the origin is obtained, leading to the conclusion that to a fair approximation the A-factors are substantially the same in each case. Furthermore, from the slopes of the lines, the differences of activation energy are found to be :

$$E_1 - E_2 = 1{\cdot}35 \text{ kcal., for propane ;}$$
$$E_1 - E_3 = 1{\cdot}74 \text{ kcal., for } iso\text{butane.}$$

These values are probably accurate to within $\pm$ 0·2 kcal. It is clear from these results that the increased rate of substitution in going from primary to secondary, and from secondary to tertiary hydrogen atoms is due to a decrease in activation energies. In what follows, therefore, we

* Also six more runs at this temperature, with results negligibly different from those given here.

shall assume that differences in rates are due entirely to differences in activation energy.

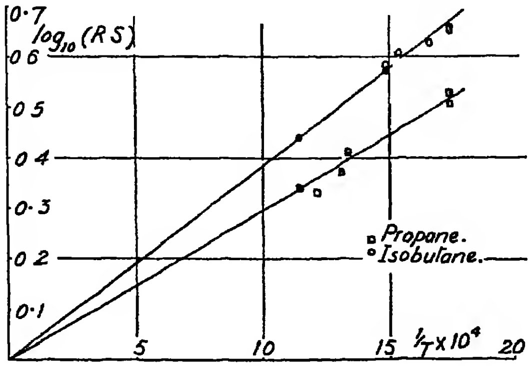

FIG. 1.

Correlation of Activation-Energy Differences with Bond-Energy Differences.—The activation-energy differences found in the last section may be compared with bond-energy differences calculated from the values given in Table I. The difference of bond-energy between primary and secondary C—H bonds in propane is 6 kcal. per mole; and if we make the reasonable assumption that the primary bonds in *n*-butane have the

TABLE III.—RELATIVE SELECTIONS AS A FUNCTION OF TEMPERATURE IN THE CHLORINATION OF PROPANE AND *Iso*BUTANE.

Hydrocarbon.	$T°$ K.	$1/T \times 10^4$.	(R.S.)	$\log_{10}$ (R.S.)
Propane	763	13·10	2·35	0·371
,, ...	573	17·44	3·2	0·505
,, ...	873	11·45	2·19	0·340
,, ...	748	13·36	2·56	0·408
,, ...	823	12·13	2·14	0·330
,, ...	573	17·44	3·35	0·525
*Iso*butane . .	673	14·86	3·71	0·569
,, . .	598	16·70	4·23	0·626
,, . .	648	15·41	4·03	0·605
,, . .	673	14·86	3·83	0·583
,, . .	873	11·45	2·76	0·441
,, . .	573	17·44	4·54	0·657
,, . .	573	17·44	4·49	0·652

same strength as the primary bonds in *iso*-butane, we have also that the difference in bond energy between the primary and tertiary bonds in *iso*-butane is 8 kcal. per mole. Using the symbol Q for the C—H bond energy we have:

$$\Delta_1^2 Q = 6{\cdot}0 \text{ kcal. per mole for propane;}$$
$$\Delta_1^3 Q = 8{\cdot}0 \text{ kcal. per mole for } iso\text{-butane.}$$

We have also, from the last section:

$$\Delta_1^2 E = 1{\cdot}35 \text{ kcal. per mole for propane;}$$
$$\Delta_1^3 E = 1{\cdot}74 \text{ kcal. per mole for } iso\text{-butane.}$$

Then if we write:

$$\Delta E = \beta \Delta Q \quad . \quad . \quad . \quad . \quad . \quad (8)$$

we find that for propane, $\beta = 0{\cdot}225$, while for *iso*-butane, $\beta = 0{\cdot}218$. These two values are substantially identical, showing that, for these hydrocarbons at least, the anticipated proportionality does exist. In view of the considerable uncertainty in the values, we shall use $\beta = 0{\cdot}22$ in further calculations.

We note that the proportionality constant β has nearly the same value as the equivalent constant α derived by Butler and Polanyi [1] when correlating the energy differences of C—I bonds in alkyl iodides and the differences of activation energies of the reaction of sodium atoms with alkyl chlorides.* These reactions are of the type:

$$Na + RCl = Na^+Cl^- + R$$

i.e., they involve an electron switch (diabatic reaction) associated with the transition from the homopolar RCl molecule to the polar Na^+Cl^-.

The relation of Polanyi and collaborators applied particularly to such cases and was derived under the following assumptions.

(1) There is no repulsion between the sodium atom and the chlorine atom in the RCl molecule when the former approaches the latter up to the transition-state configuration. The necessary energy for the reaction is given entirely by the extension of the RCl bond.

(2) There is no appreciable resonance in the transition state so that on a potential-energy plot the activation energy is given to a good approximation by the crossing-point of the extension curve of the RCl molecule and the repulsion curve of the Na^+Cl^- molecule and the radical R.

It is important to note that the present reactions are in an entirely different class. They must be classed as adiabatic, and resonance in the transition state is to be expected to play an important role; assumption (2) therefore cannot apply. Reactions of this type, viz.:

$$Cl + HR = HCl + R$$

have been treated by the semi-empirical method of Eyring. In particular, based on this method, Hirschfelder [7] derived a simple equation identical in form to that of Polanyi and Butler relating bond strength of the bond to be broken to activation energies, for three-atom reactions of this type. The proportionality constant was found to have a value of about 0·055, about 1/5th of that found for the reactions of alkyl halides with sodium and about 1/4th of that found in the present case. This relation of Hirschfelder refers to the absolute value of the activation energies, whereas the Polanyi and Butler equation and that used here apply to differences of activation energies of closely related reactions. Though there is no reason to expect that the proportionality constants for the absolute values of activation energies (Hirschfelder formula) and that for the present differences of activation energies should be identical, the differences in order of magnitude are surprising. It is clear that in relation to the differences in bond strength the differences in activation energy are very much greater than the relation between bond strength and the absolute values of the activation energy would lead one to expect.

The fact that the proportionality constant in the present case is not very much smaller than that found by Butler and Polanyi leads one to the following conclusion. If the method of plotting potential energies against extension of the R—H bond is adopted, the course of the reaction can, according to Evans and Polanyi,[4] be pictured as given in Fig. 2. Here I_1 and I_2 refer to the extension curves of two R—H bonds of different

* The fact that the bond strengths of C—I bonds are compared with reactions of alkyl chlorides, i.e. C—Cl bonds instead of C—I bonds, has been justified by Butler and Polanyi,[1] who showed that a graduation of the C—Cl bond strengths in these alkyl halides should be identical with that of the corresponding C—I bonds.

[7] Hirschfelder, *J. Chem. Physics*, 1941, 9, 645.

strength, the chlorine atom being pushed into the position which it would assume in the transition complex. These curves are displaced from the normal extension curve of the R—H bond by the amounts S_1 and S_2, which correspond to the energy of repulsion of the chlorine atom and the RH molecule. The repulsion curve of HCl and R is represented by curve II and is assumed to be identical in both cases. The dotted curve represents the actual reaction path, taking account of the lowering of the activation energy due to resonance. The activation energy is then given by:

$$E = S + B - R,$$

where S = repulsion energy,
B = bond-extension energy,
and R = resonance energy.

For the difference of two activation energies we have:

$$\Delta E = \Delta S + \Delta B - \Delta R.$$

Now if it is assumed that ΔS and $-\Delta R$ are either small and negligible, or are of similar value and therefore cancel each other, we find that

$$\Delta E \approx \Delta B,$$

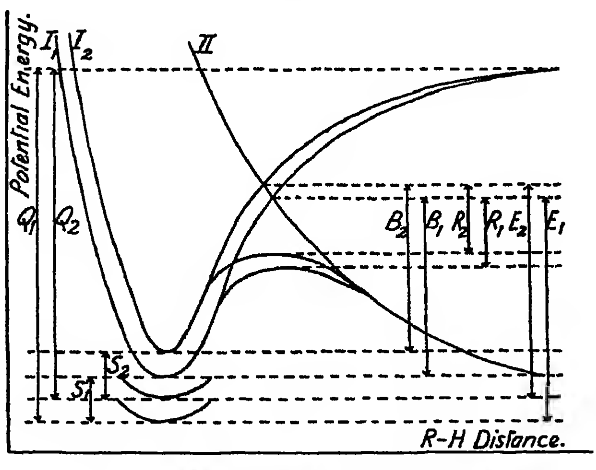

FIG. 2.—Potential Energy Diagrams of Systems.
R_1 . . H . . . Cl and R_2 . . . H . . . Cl

namely, that the difference in activation energy is due mainly to the difference in extension of the bond, which is the result arrived at by Polanyi, and which leads to his proportionality factor of 0·27 between bond energy and activation energy. The fact that in our case a value not much smaller than this was found must mean either that the differences in repulsion energy and resonance energy in going from substitution at a primary carbon atom to that at a secondary atom are small, or that these terms cancel each other.

A Further Extension of the Correlation of Bond Energy and Activation Energy Differences.—It has been shown in the last section that from Hass' results where data are available over a range of temperature, there is obtained the same value of β in either of the cases considered. It is also clear that in these two cases the ratio of the temperature-independent factors in the rate equations for substitution in the different positions is approximately unity. If we assume that these values still hold for the other hydrocarbons given in Table II, we may extend the calculations

accordingly. The hydrocarbons concerned are butane, pentene, *iso*-pentane and pentane, where, in each case, data exist for substitution at one temperature only.

$$\frac{k_2}{k_1} = \frac{A_2}{A_1} e^{(E_1 - E_2)/RT} \quad . \quad . \quad . \quad . \quad (9)$$

Assuming, as indicated above, a value of unity for A_2/A_1, this becomes :

$$\log_{10} \frac{k_2}{k_1} = \log_{10} (\text{R.S.})_{2^\circ, 1^\circ} = \frac{E_1 - E_2}{2{\cdot}303\, RT} \quad . \quad . \quad (10)$$

For butane from Table II, $(\text{R.S.})_{2^\circ, 1^\circ} = 3{\cdot}19$, and $T = 573^\circ$ K. Substitution of these values in eqn. (10) yields the result :

$$\Delta_1{}^2E = 1{\cdot}33 \text{ kcal. per mole.}$$

We are now unable to proceed along the same lines as before, to obtain a value of $\Delta E/\Delta Q$, because there is no value available for the energy of the secondary C—H bond in butane. However, the reverse procedure can be made to give such a value. Using eqn. (8), and a value of $\beta = 0{\cdot}22$, we find a value $\Delta_1{}^2Q$ of 6·0 kcal. per mole. Combining this with the value of 94·0 kcal. per mole for the primary C—H bond strength in butane, as given in Table I, we obtain a value of 88·0 kcal. per mole for the corresponding secondary bond strength. While it is not possible to make any direct estimation of the accuracy which may be expected of this value, we may at least observe that it falls naturally into the sequence of values given in Table I, and is to this extent convincing.

We may proceed in an analogous manner to find the differences in activation energy in the cases of the two pentanes given in Table II. There are also data for "pentene," but since the nature of the isomer is not stated, calculations would be of no value.

Applying the same methods to the pentanes, we obtain the following results :

for *n*-pentane : $\Delta_1{}^2E = 1{\cdot}11$ kcal. per mole ;
for *iso*-pentane : $\Delta_1{}^2E = 1{\cdot}10$ „ „
for *iso*-pentane : $\Delta_1{}^3E = 1{\cdot}67$ „ „

Using eqn. (8) and the same value of β as before, we thus find for the differences in bond energies :

for *n*-pentane : $\Delta_1{}^2Q = 5{\cdot}0$ kcal. per mole ;
for *iso*-pentane : $\Delta_1{}^2Q = 5{\cdot}0$ „ „
for *iso*-pentane : $\Delta_1{}^3Q = 7{\cdot}5$ „ „

These last results show that the differences found for the pentanes are slightly but distinctly lower than the corresponding differences for the four and three carbon-atom molecules.

The results do not permit the calculation of absolute bond-energy values, as in the case of butane, since there are no data available for the primary C—H bond strength in *n*- or *iso*-pentane. In the following section we shall, however, derive an empirical relation which allows one to estimate that quantity.

Extrapolated Bond Energies.—An examination of the bond-energy values given in Table I shows that in passing along the series of normal paraffins, not only do the absolute values of the C—H bond energies decrease, but there is also a fall in the differences between successive values, indicating the existence of an asymptotic limit to the bond energy as the number of carbon atoms in the chain is increased indefinitely. An empirical relation representing with fair accuracy the results for the primary C—H bonds in normal paraffins was found as follows :

$$Q_n = Q_0 + A \,.\, 1/n \quad . \quad . \quad . \quad . \quad (11)$$

where Q_n is the energy of the primary $C—H$ bond of the paraffin with n carbon atoms, Q_0 is the limiting value $\lim_{n\to\infty} Q_n$, and A is a constant. Fig. 3 shows a plot of the value of Q_n, as taken from Table I, against the reciprocal number of carbon atoms. A reasonable straight line is obtained, indicating an asymptotic limit of about 91·5 kcal. per mole. It is to be noted that this value is only about 2·5 kcal. per mole lower than the value for n-butane, a much smaller decrease than is observed in passing from

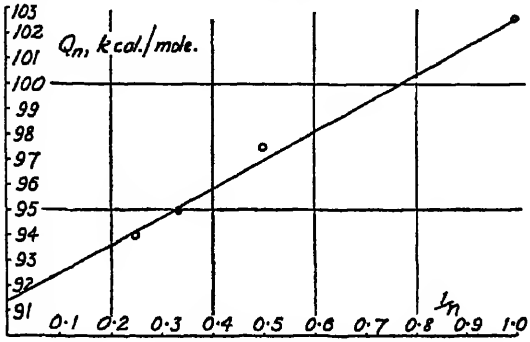

Fig. 3.

methane to n-butane. For the present discussion we require the value of 93·5 kcal. per mole obtained from Fig. 2 for the bond energy of the primary C—H link in n-pentane.

Some Further C—H Bond-Energy Values—Having now a value for the energy of the primary C—H bond in n-pentane and assuming, as was done for the butanes, the same value for the same bond in *iso*-pentane, we may make further use of the bond-energy differences for the pentanes,

TABLE IV.

Summary of Calculated Bond Strengths.

Paraffin.	C—H Bond.	Strength. kcal. mole.
n-butane .	Secondary	88·0
n-pentane .	Primary	93·5
,, .	Secondary	88·5
iso-pentane .	,,	88·5
,, .	Tertiary	86·0

derived earlier. Use of these values gives the following additional bond energies:

secondary bond in n-pentane: 88·5 kcal. per mole.
,, ,, *iso*-pentane: 88·5 ,, ,,
tertiary ,, ,, 86·0 ,, ,,

We may note that the secondary bonds in n- and *iso*-pentane have substantially the same energy as the corresponding bond in n-butane, a value only 1·0-1·5 kcal. per mole less than that for the secondary C—H bond in propane. We have also a similar equality between the energies of the tertiary bonds in *iso*-pentane and *iso*-butane. The energy changes in passing along the series are thus seen to be very small in these cases, a state of affairs which is naturally to be expected by comparison with

the results given for the series of primary bonds. The effect of increasing the number of carbon atoms is to decrease the secondary C—H bond energy, just as the primary C—H bond energy is decreased, but to a lesser extent. In the case of tertiary bonds, only two being available, no decrease is observed.

In conclusion, it is convenient to summarise in tabular form the various additional bond strengths calculated in this paper. These data are given in Table IV, where the results are given without reference to the method by which they have been derived.

Résumé.

On discute les expériences de substitution du chlore dans les hydrocarbures saturés. On sait que la réaction est une réaction en chaîne, dont la vitesse est déterminée par l'attaque de la paraffine par l'atome de chlore. On démontre ici que, lorsqu'un certain nombre de produits résultent de la substitution d'atomes d'hydrogène liés à différents atomes de carbone, les vitesses relatives de réaction des atomes de chlore avec les différents atomes d'hydrogène peuvent être calculées à partir des rendements relatifs en produits résultants. Les différences dans les vitesses de réaction sont attribuées principalement aux différences d'energie d'activation, qui suivent l'ordre : primaire > secondaire > tertiaire. Ces dernières sont reliées aux différences correspondantes des énergies de liaison. A leur tour, les différences de forces de liaison sont estimées à partir des différences d'énergies d'activation.

Zusammenfassung.

Die Substitution von Chlor in gesättigten Kohlenwasserstoffen wird besprochen. Es ist bekannt, dass dies eine Kettenreaktion ist, deren Geschwindigkeit vom Angriff des Paraffinmoleküls durch ein Chloratom bestimmt wird. Es wird nun gezeigt, dass, wenn eine Reihe von Produkten durch Substitution an verschiedenen Kohlenstoffatomen entstehen, die relative Geschwindigkeit der Reaktion an verschiedenen Stellen aus der Zusammensetzung der Produkte berechnet werden kann. Die Geschwindigkeitsunterschiede werden hauptsächlich Unterschieden in der Aktivierungswärme (primär > sekundär > tertiär), die mit den entsprechenden Differenzen in den Bindungsenergien im Zusammenhang stehen, zugeschrieben. Andererseits können Differenzen in der Bindungsstärke aus den Unterschieden zwischen den Aktivierungswärmen berechnet werden.

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THE STRUCTURE OF METHYLENE.

BY R. G. W. NORRISH AND G. PORTER.

Received 14*th August*, 1947.

The occurrence, stability and chemical behaviour of methylene has been a matter of much conjecture since Nef, in a series of papers between 1892 and 1897, described over a hundred compounds of bivalent carbon. It has been frequently pointed out on theoretical grounds that methylene might be considered as the simplest organic compound and one with the properties of a physically and chemically stable molecule arising from a ^3P carbon atom. On the other hand it has often been postulated as a highly reactive intermediate in many organic reactions, with the nature of a free radical. It is our purpose to review the evidence in the light

of some new data and to attempt to decide which of the above gives the better description of the known properties of methylene.

Occurrence.

The existence of methylene is now well established, the first proof having been obtained by Norrish, Crone and Saltmarsh [1] from the photochemical decomposition of ketene which was shown to decompose on the absorption of light in the region 2600 A. to 3850 A. according to the equation:

$$2\ CH_2CO \rightarrow C_2H_4 + 2\ CO$$

the primary change being rupture at the olefinic bond to give methylene and carbon monoxide. Ross and Kistiakowsky [2] found that the quantum yield in the region of maximum absorption was near to unity and concluded that the ethylene was formed by bimolecular collision of two methylene radicals. Norrish and Kirkbride [3] showed that diazomethane behaved similarly on photolysis, the primary split being into methylene and nitrogen. Bawn and Dunning [4] have concluded that methylene is also obtained from the reaction $2Na + CH_2X_2 \rightarrow CH_2 + 2NaX$, ethylene again being the final product.

The occurrence of methylene in the thermal decomposition of hydrocarbons, in particular methane, is still controversial; it was reviewed at a Discussion of this Society in 1939 [5] and will not be considered further here, except in so far as it throws light on the structure of CH_2.

The most direct evidence of the existence of methylene is derived from experiments using the Paneth-mirror technique. Paneth himself made several unsuccessful attempts to prepare and detect methylene,[6] his failure possibly being due to the unsuitability of the detectors (carbon and benzoic acid) which he used. Rice and his co-workers, in a long series of experiments on the thermal decomposition of hydrocarbons, found that only alkyl radicals could be detected. They subsequently detected methylene in the decomposition products of diazomethane [7] and found that it had a half-life similar to the alkyl radicals, and at higher temperatures reacted to give methyl. Belchetz and Rideal reported methylene radicals in the thermal decomposition of methane [8] and concluded that they reacted in about 10^{-7} sec. to give methyl. Pearson, Purcell and Saigh [9] obtained methylene from the photochemical and thermal decomposition of diazomethane and the photochemical decomposition of ketene. They detected it by the mirror method, analysed the products and made a detailed study of its properties.

The occurrence of methylene is thus well established. It remains to see what information the experimental data give us about its structure.

The Reactions of Methylene.

(a) With Itself.—Methylene reacts with other methylene radicals to give ethlyene, and it is in connection with this reaction that the strongest evidence of its stability compared with other free radicals has been found. In the work mentioned above, Pearson and his co-workers found that although the half-life of methylene in diazomethane was 5×10^{-3} sec., in ketene it had a much greater half-life which, although not measured, was greater than 0·1 sec. They concluded

[1] Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1933, 1533.
[2] Ross and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, 56, 1112.
[3] Norrish and Kirkbride, *J. Chem. Soc.*, 1933, 119.
[4] Bawn and Dunning, *Trans. Faraday Soc.*, 1939, 35, 185.
[5] Barrow, Pearson and Purcell, *ibid.*, 880.
[6] Paneth and Lautsh, *J. Chem. Soc.*, 1935, 380.
[7] Rice and Glazebrook, *J. Amer. Chem. Soc.*, 1934, 56, 2381.
[8] Belchetz and Rideal, *ibid.*, 1935, 57, 1168.
[9] Pearson, Purcell and Saigh, *J. Chem. Soc.*, 1938, 409.

that methylene is to be regarded as a highly reactive molecule formed from bivalent carbon rather than as a free radical in the sense that methyl is. In view of the importance of this conclusion we have repeated these experiments on the photolysis of ketene and as described below have confirmed that radicals are liberated which may have a relatively long life. However, comparison experiments with acetone have shown that the methyl radical has a lifetime of the same order, under the same conditions and that the lifetimes of both radicals may be varied within wide limits by varying the conditions of the experiments.

Experimental.

Ketene was prepared by the pyrolysis of acetone at 700° c.[10] and carefully fractionated between three traps at − 105°, − 130° and − 187° until further fractionation effected no separation and all the distillate collected in the middle trap. Vapour-pressure determinations at several temperatures gave values agreeing closely with those of Pearson, Purcell and Saigh. Our apparatus was similar to theirs ; in the first experiments a quartz tube 11 mm. diam. and water-cooled at the illuminated part, was used, the rate of flow was 12 m./sec. and the pressure 1·5 mm. Hg measured by Bourdon gauge, all mercury being eliminated from the apparatus. Our light source was a 7½ kw. high-pressure mercury-vapour lamp in a searchlight holder with aluminium reflector which, with an additional quartz lens, gave a sharp focus about 2 cm. diam. of very high intensity.

It was found that tellurium mirrors were readily removed even in the cold, though in the quantitative experiments they were heated to about 80° to prevent polymer formation. Several methods of making standard mirrors were tried. The first consisted of condensing the metal on to a weighed glass rider controllable magnetically, reweighing and revolatilising on to the tube. By this method it was found that of the ketene passed, 0·003 % decomposed to give free radicals. The times required to remove a weighable amount were inconveniently long and the method used in obtaining the results below was to make a mirror on the tube longer than a standard comparison mirror, and take the time from its reaching standard length to complete removal. Although this was not capable of any greater accuracy than was obtained by previous workers it had the advantage that any errors due to incomplete "clean-up" ahead of the mirror were eliminated.

It was soon apparent that the radicals obtained in this manner decayed fairly rapidly along the tube, the following results being obtained in the order given :

Distance of mirror from light source (in cm.)

70 67 68 17 18 70 57 55·5 60 74·5 26 35·5 90 95 23 11·5

Time of removal of mirror (in sec.)

480 535 510 260 257 485 395 395 405 545 235 360 900 900 270 220

As a check the experiments were now repeated, with carefully refractionated acetone and with the flow conditions as nearly as possible identical with those above. The following results were obtained :

Distance of mirror from light source (cm.)

74·5 15·5 74·5 16 36·5 31·5 49·5 10 89 18 92·5

Time of removal of mirror (sec.)

337 122 337 118 196 182 305 90 430 130 430

Taking the activity A of methylene as inversely proportional to the time of removal of the mirror we find that these results show some deviation from the unimolecular law. The half-life time at 30 cm. from the light source calculated from the equation $t_{\frac{1}{2}} = \dfrac{0{\cdot}30(t_2 - t_1)}{\log A_1 - \log A_2}$ is 35×10^{-3} sec. for ketene and 22×10^{-3} sec. for acetone.

Thus in our apparatus the half-life of methylene in ketene was not very much longer than the half-life of methyl in acetone under the same conditions. The experiments were now repeated under a variety of conditions. Pyrex tubes were used in place of quartz, the rate of flow, pressure, concentration and method of cleaning the tube were varied and different metals were used, but in the course of nearly two hundred experiments with many samples of ketene and acetone no great difference between their respective half-lives was found, although the half-life of both was changed considerably by altering the conditions. The main factor influencing the lifetime of the radicals seemed to be concentration. The

[10] Hurd and Tallyn, *J. Amer. Chem. Soc.*, 1925, 47, 1427.

curves in Fig. 1 and Fig. 2 are plotted from the results obtained with ketene and acetone respectively in a longer tube, using a rate of flow of 2·5 m./sec. The concentration of radicals was less than above, the mirror removal times being between 7 and 70 min. The activity *A* is put equal to the reciprocal mirror-removal time in min. × 100.

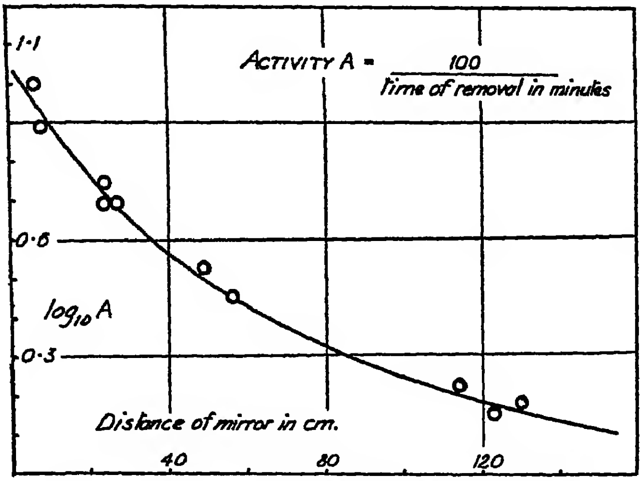

FIG. 1.—Unimolecular decay curve for methylene.

It is apparent from these curves that there is considerable departure from the unimolecular rate law and that the lower concentration of radicals has increased

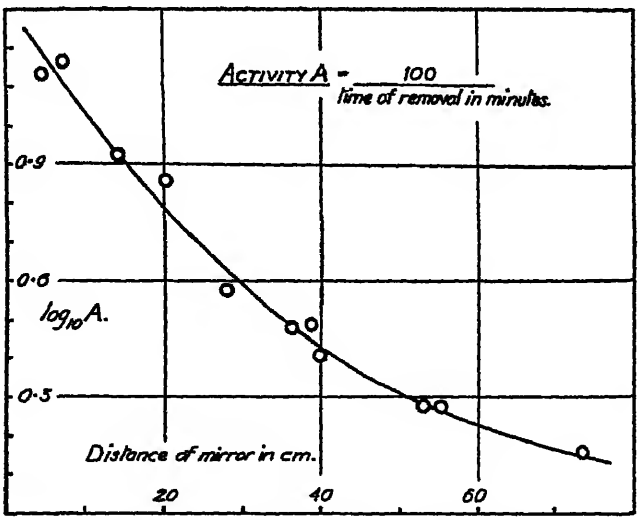

FIG. 2.—Unimolecular decay curve for methyl.

their lifetime in both cases. Taking points of equal concentration on these curves we get for the "unimolecular" half life-time:

half-life of methyl at 20 cm. = 60×10^{-3} sec.
half-life of methylene at 20 cm. = 130×10^{-3} sec.

and for a lower concentration:

half-life of methyl at 60 cm. = 190×10^{-3} sec.
half-life of methylene at 100 cm. = 400×10^{-3} sec.

Thus the half-life of methylene has been extended to the same order as was found by Pearson but the half-life of methyl under the same conditions has also been extended to half this value.

It is difficult to predict what will be the effect of concentration under the conditions of stream-lined flow which hold in these experiments but other workers also have found that the half-life of radicals could be varied within wide limits by quite small concentration differences. Thus Pearson found that the half-life of methylene in diazomethane at 2 mm. pressure was extended from 5×10^{-3} to 250×10^{-3} by the addition of only 2 mm. of nitrogen and Paneth [12] found that the half-life of methyl in helium and a heated tube was 0·1 sec. and concluded "We have no doubt that under still more favourable conditions the existence of free methyl might be prolonged still further."

It is thus very important when comparing the lifetimes of radicals in flow systems to do so under identical conditions. When this is done the radicals obtained from ketene and acetone photolysis are found to have similar half-lives, the half-life of methylene in our experiments being about twice that of methyl. The fact that the lifetime varies over such wide limits with different conditions of concentration, etc., would explain why Pearson and his co-workers obtained different values for the two radicals, the work on acetone having been carried out several years previously to that on ketene.

The great similarity between the two radicals in the above experiments and also in their reactivity with metals (see below) raises the question whether we are actually dealing with the same radical in both cases due to disproportionation reactions such as:

$$2\,CH_3 \rightarrow CH_2 + CH_4$$
$$2\,CH_2 \rightarrow CH_3 + CH$$
$$CH_2 + CH_2CO \rightarrow CH_3 + CHCO\text{, etc.}$$

There is strong evidence that this is not the case. Firstly, the hydrocarbons formed are almost exclusively ethylene with ketene,[1, 13] and ethane and other unsaturates with acetone.[14 15] Secondly, an analysis of the products formed with tellurium gave methyl tellurides with acetone [16] and tellurformaldehyde with ketene [8] and thus it is well established that we are in fact dealing with the methyl and methylene radicals respectively.

We may therefore conclude from these experiments that the reactions of methyl and methylene radicals with themselves occur with similar readiness under the same conditions.

(*b*) **Reaction with Hydrogen.**—Bawn and Milstead,[17] using methylene formed from the reaction of sodium on methylene halides, found that at 300° methane was formed and suggested the reaction: $CH_2 + H_2 \rightarrow CH_4$, whereas Rosemblum [18] using methylene from the photolysis of ketene found a high proportion of saturated hydrocarbons including polymers and favoured the reaction

$$CH_2 + H_2 \rightarrow CH_3 + H.$$

Using the results of Rosenblum, Wicke [20] has estimated an activation energy of 4 ± 2 kcal. for this reaction. In any case, the reaction with hydrogen must proceed readily as it occurs almost to the exclusion of the production of ethylene by three-body radical recombination which, as we have already seen, is a rapid reaction.

(*c*) **Reactions with Hydrocarbons.**—There appears to be little doubt that the reaction of methylene with hydrocarbons proceeds very rapidly. According to several independent authors it reacts with ethylene [13, 18] and ethane [18] to give polymers, and with methane,[19, 8, 13] though there is some doubt about the activation energy here, the highest estimate being 12 ± 5 kcal.[19] Rice found in his experiments on the thermal decomposition of hydrocarbons that only alkyl radicals came out of the furnace and concluded that methylene must react readily with hydrocarbons to give methyl.

(*d*) **Reactions with Metals.**—The reactions of both methyl and methylene

11 Pearson and Purcell, *J. Chem. Soc.*, 1934, 1718.
12 Paneth, Hofeditz and Wunsch, *ibid.*, 1935, 372.
13 Rosenblum, *J. Amer. Chem. Soc.*, 1941, **63**, 3322.
14 Damon and Daniels, *ibid.*, 1933, **55**, 2363.
15 Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1934, 1456.
16 Pearson and Purcell, *ibid.*, 1935, 1151.
17 Bawn and Milsted, *Trans. Faraday Soc.*, 1939, **35**, 889.
18 Burton, Davis, Gordon and Taylor, *J. Amer. Chem. Soc.*, 1941, **63**, 1956.
19 Rice and Dooley, *ibid.*, 1934, **56**, 2747.

radicals with metallic mirrors occur very readily, nearly every collision resulting in reaction. Both react at room temperature. Furthermore, in our experiments on the photochemical decomposition of ketene described above, we have been unable to find any difference in reactivity of the methylene and methyl radicals with different metals unlike Rice who, using methylene obtained from the pyrolysis of diazomethane, found [7] that some metals were specific to alkyl radicals and not removed by methylene. We have found that selenium, tellurium, antimony and bismuth mirrors were all readily removed and as bismuth was one of the metals found by Rice to be specific to methyl the half-life times of both radicals were estimated using bismuth mirrors. The same values were obtained as with tellurium under the same conditions, the time of removal of mirrors of the same density being about three times as long for bismuth in both cases. Lead and zinc mirrors were equally difficult to remove by both radicals.

(*e*) **Reactions with other Compounds.**—Reactions of methylene with carbon monoxide,[21] diazomethane,[3, 9] and ethylene oxide [22] have been described. The activation energy of its reaction with oxygen has been assessed at 2 kcal.[23] and with ether at 15 ± 5 kcal.[24] With nitric oxide very little reaction occurred [18] but this may be because CH_2NO, unlike CH_3NO, is still a free radical and reacts further or is unstable.

Discussion.

The above review of the reactions of methylene gives no indication that it behaves in any way differently from the known free radicals and a comparison of activation energies, when these are available, with those for similar reactions of methyl and in particular a comparison of the reactions of these two radicals with themselves shows a close parallelism. Thus, as far as its chemical behaviour is concerned, methylene is best described as a free radical.

There is nothing in the photochemical data which conflicts with this view. The photochemical decomposition of ketene occurs at a maximum wavelength of 3850 A.[1] corresponding to an energy of 74 kcal./g. mole. This is not sufficient to break the C=C bond but, as pointed out by Norrish, Crone and Saltmarsh, the energy of reorganisation of the CO radical to carbon monoxide is sufficient to provide the extra energy without any additional energy of reorganisation of CH_2.

Theoretical considerations have indicated that the lowest energy state of methylene is one with paired spins arising from bivalent carbon. Thus Lennard-Jones [25] calculated from group theory that the lowest energy state was a singlet and Mecke [26] calculated from thermal and spectroscopic data that the first hydrogen in methane required the greatest energy for removal and predicted a greater stability for CH_2 than CH or CH_3. Voge,[27] on the other hand, calculated wave-mechanically that the energies of removal of successive hydrogen atoms from methane should be almost constant but this is now known to be incorrect the first requiring 101 kcal.[28] and the last 80 kcal.[29]

There are two possible explanations of the free-radical behaviour of methylene. The first is that the free-radical structure is actually the most stable as the energy difference from the molecular structure is very small due to the energy of promotion of the carbon atom from the triplet to the quintet state being offset by the extra bonding energy of the two C—H bonds in the triplet structure. This may be quite large, as in the

[20] Wicke, *Die Chemie*, 1945, 58, 16.
[21] Staudinger and Kupfer, *Ber.*, 1912, 45, 508.
[22] Fletcher and Rollefson, *J. Amer. Chem. Soc.*, 1936, 58, 2135.
[23] Gregory and Style, *Trans. Faraday Soc.*, 1936, 32, 724.
[24] Rice and Glazebrook, *J. Amer. Chem. Soc.*, 1933, 55, 4329.
[25] Lennard-Jones, *Trans. Faraday Soc.*, 1934, 30, 70.
[26] Mecke, *Z. physik. Chem. B*, 1930, 7, 108.
[27] Voge, *J. Chem. Physics*, 1936, 4, 581.
[28] Kistiakowsky and Van Artsdalen, *J. Chem. Physics*, 1944, 12, 469.
[29] Herzberg, *Molecular Spectra and Molecular Structure* (New York, Prentice Hall), Vol. I.

singlet state we are dealing with bonds arising from a pure p carbon atomic orbital, whereas the bonds in the triplet structure can be sp digonal hybrids. The CH radical with bond strength 80 kcal. gives an example of the former type and this is much weaker than sp hybrid bonds, the tetragonal hybrid having a bond strength of about 101 kcal.[28] Further there is some evidence that the digonal hybrid bond is the strongest of the three sp hybrids; thus the C—H bond length increases and the stretching force constants decrease in the series, $C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$,[30] and Cherton [31] has found from absorption-limit data that the dissociation energy of the C—H bond in acetylene is as high as 121 kcal. This question is considered further by Walsh in this Discussion. A recent estimate of the energy of promotion of carbon to the quintet state of 65 kcal.[32] is comparable with the extra bonding energy obtained in this way, but the inaccuracy of the above data prevents us from drawing any quantitative conclusions.

The second possibility is that the energy difference between the two states of methylene may be quite large but that in all the photochemical and thermal processes considered, it is liberated in the promoted state and has a very low transition probability to the singlet structure. Strong evidence that this is the more probable state of affairs is that of Bawn and Dunning [4] who found that the sodium D radiation was emitted when sodium reacted with methylene halides and could only explain this as arising from the reaction, $Na + —CH_2X \rightarrow CH_2 + NaX$, the difference between the exothermicity of this reaction and the energy of the light quantum being furnished by the instantaneous transition of CH_2 to the singlet state. This would require a minimum energy between the two states of 27 kcal.

Spectroscopic evidence is almost completely lacking. A spectrum found in comets and later in the laboratory [33, 34] and tentatively assigned to methylene would give an H—C—H bond angle of 140°, intermediate between the linear triplet and right-angled singlet structures but as it was obtained in emission it can in any case tell us little about the ground state of methylene. We have made several unsuccessful attempts to obtain the methylene spectrum in absorption using flow methods and an intense light source and it is probable that a final elucidation of its structure will have to be made in this way. Until such evidence is forthcoming the chemical properties of methylene liberated in photochemical and thermal experiments lead us to the conclusion that it behaves like any other free radical with unpaired spins and is best described as such.

Summary.

We have studied the properties of methylene obtained from the photolysis of ketene using the metallic-mirror technique, and find that its chemical behaviour is very similar to that of the methyl radical obtained by photolysing acetone and used in comparison experiments. In addition an examination of the other reactions of methylene shows a reactivity in every way comparable with other free radicals. Although the subject is far from settled it appears probable that methylene is normally liberated in the promoted state or is easily activated to it. In any case, from its chemical behaviour, methylene as normally found in photochemical and thermal reactions is best described as a free radical.

Résumé.

On a étudié les propriétés du méthylène, obtenu dans la photolyse du cétène par la technique du miroir; le comportement chimique est semblable à celui

[30] Gordy, *J. Chem. Physics*, 1946, 14, 305.
[31] Cherton, *Bull. Soc. Sci., Liége*, 1942, 11, 203.
[32] Long and Norrish, *Proc. Roy. Soc., A*, 1946, 337.
[33] Herzberg, *Astrophys. J.*, 1942, 96, 314.
[34] Herman, *Compt. rend.*, 1946, 223, 280.

du radical méthyle obtenu par photolyse de l'acétone. La réactivité du méthylène est comparable à celle d'autres radicaux libres. Il est probable que le méthylène est normalement libéré à l'état activé ou est facilement activé.

Zusammenfassung.

Die Eigenschaften von durch Photolyse von Keten erhaltenem Methylen sind mit Hilfe der Spiegelmethode untersucht worden. Das chemische Verhalten ähnelt dem des bei der Photolyse von Aceton gewonnenen Methylradikals. Die Reaktivität des Methylens ist mit der anderer freier Radikale vergleichbar. Es ist wahrscheinlich, dass Methylen normalerweise in angeregtem Zustand gebildet wird oder leicht zu diesem aktiviert wird.

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THE REACTION OF FREE ALKYL RADICALS IN THE GAS PHASE.

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There is considerable evidence that the thermal and photochemical decomposition of hydrocarbons involves the reaction of atoms and radicals. A knowledge of the reactions by which these simple entities are consumed is necessary in order to formulate the overall mechanism of the decomposition reaction. Whilst there have accumulated some reliable data on the nature and activation energy of these reactions, much of this information is obtained by indirect methods, such as the analysis of the mechanism of a complex change. It is of obvious importance that the rates of these reactions should be obtained by more direct and independent methods. Numerous studies [1] have shown that free radicals may be produced in the homogeneous gaseous reactions of organic halides with sodium atoms in accordance with the general reactions:

$$\mathrm{R\,Hal} + \mathrm{Na} \longrightarrow \mathrm{Na\,Hal} + \mathrm{R}- \quad . \quad . \quad (1)$$
$$\mathrm{R\,Hal_2} + 2\mathrm{Na} \longrightarrow 2\mathrm{Na\,Hal} + \mathrm{R}< \quad . \quad . \quad (2)$$

By using excess atomic sodium, the radical may be prepared in the absence of any reactive substance, and thus the method is applicable to the detailed study of the interaction of radicals amongst themselves and with other molecules.

In the present work reactions (1) and (2) have been used to prepare methyl, ethyl and methylene radicals. The products and activation energies of the disproportionation reactions of the radicals and their reactions with molecular hydrogen have been measured.

Experimental.

The experimental method was essentially the same as that used previously.[1c] Two reaction vessels were employed, (*a*) a spherical vessel of 5 l. capacity, and (*b*) a cylindrical vessel of 7 cm. diam. The temperature of the sodium "boat" was maintained constant in all experiments at 300° C. In determining the material balance of a "run", a known weight of halide was introduced into the halide trap (in a sealed capsule), and the experiment continued until all the halide had been consumed. The product gases were separated and analysed as described previously.[1c]

[1a] Polanyi, Horn and Style, *Trans. Faraday Soc.*, 1934, **30**, 189; [b] Allen and Bawn, *ibid.*, 1938, **34**, 463; [c] Bawn and Milsted, *ibid.*, 1939, **35**, 889.

Methylene Radicals.

Methylene radicals were formed homogeneously by the reaction of methylene bromide with a large excess of sodium atoms:

$$Na + CH_2Br_2 \longrightarrow NaBr + CH_2Br^- + 10{\cdot}7 \text{ kcal.} \quad (3)$$
$$Na + CH_2Br^- \longrightarrow NaBr + CH_2 \quad (4)$$

Previous investigations [2] showed that reaction (4) was highly chemiluminescent, the luminescence corresponding to the D line of sodium. This requires a minimum energy of 48·6 kcal., and could only arise if reaction (4) were exothermic to this extent. If the methylene produced in (4) were in the biradical state, the exothermicity of the reaction would be about 10 kcal. and thus the necessary energy to excite the sodium must be supplied by a change in the valence state of carbon from quadrivalent in the $.CH_2Br^-$ or $> CH_2$ radical to the divalent state in methylene. It may be concluded, therefore, that the methylene is produced in a singlet state and thus has the nature of a reactive molecule rather than that of a free radical.

Methylene in Nitrogen.—The gaseous products from methylene formed in nitrogen gas (4-8 mm. pressure) at 300-360° c. were, under all experimental conditions, a mixture of ethylene and methane. No ethane or other hydrocarbons were formed. Fig. 1A shows the variation of the logarithm of the methane/ethylene volume ratio with temperature at constant nitrogen pressure. The material balance of the reaction, that is, the amount of hydrocarbon formed corresponding to the methylene formed, as determined by the amount of CH_2Br_2 used, showed that at the nitrogen pressures of 7-8 mm. and temperature around 300° c., about 88 % of the carbon appeared as methane and ethylene. At lower pressures or higher temperatures the yield dropped to 60-70 %. The ethylene was formed by dimerisation of the methylene,

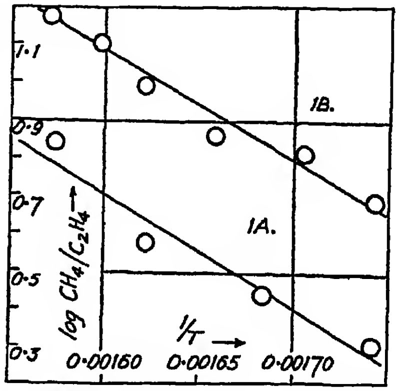

FIG. 1A.—Methylene in nitrogen. $p_{N_2} = 5{\cdot}5$ mm.

FIG. 1B.—Methylene in hydrogen. $p_{H_2} = 6{\cdot}2$ mm.

$$CH_2 + CH_2 \longrightarrow C_2H_4 \quad (5)$$

and since the percentage increased sharply with increase in inert gas pressure, it may be assumed that the reaction occurred in the gas phase by a triple-body mechanism. The methane might have been formed by reaction between the radicals in one stage, viz.

$$CH_2 + CH_2 \longrightarrow CH_4 + C \quad (6)$$

or as the two-stage process,

$$CH_2 + CH_2 \longrightarrow CH_3 + CH \quad (7)$$
$$CH_3 + CH_3 \longrightarrow CH_4 + CH \quad (8)$$

The former process is the more probable as it is unlikely that reaction (7) occurred, since a careful search failed to show the presence of ethane in the products, as would have been expected if methyl radicals had been produced. In spite of the relatively low carbon yield as CH_4 and C_2H_4, all the hydrogen initially introduced as methylene appeared in these hydrocarbons. This strongly supports the view that methane was formed entirely by reaction (6). The results showed that the percentage carbon deficiency in the products was of the same order as that required by the production of carbon in reaction (6). This reaction has also been postulated by Williamson,[8] who, in the thermal decomposition of ketene at 530-550° c., obtained CO, CH_4 and a deposit of carbon. He suggested the initial reaction, $CH_2CO \longrightarrow CH_2 + CO$, followed by (6).

[2] Bawn and Dunning, *Trans. Faraday Soc.*, 1939, **35**, 185.
[8] Williamson, *J. Amer. Chem. Soc.*, 1934, **56**, 2216.

The overall activation energy of the reaction calculated from Fig. 1A is 14·0 kcal. This is the difference between the activation energies of reactions (6) and (5). No data exist on the activation energies of these reactions, but (5) is highly exothermic and it is unlikely that this simple association reaction requires an activation energy. The measured activation energy of 14·0 kcal. may be assumed, therefore, to refer to the reaction

$$CH_2 + CH_2 \longrightarrow CH_4 + C.$$

The possibility that this reaction occurred on the surface of the vessel cannot be excluded at present.

Methylene in Hydrogen.—In hydrogen gas the products of the reaction of methylene were the same as in nitrogen, viz. methane and ethylene. The ratio, CH_4/C_2H_4, was higher than in nitrogen and a loss of hydrogen from the carrier gas, which amounted to 25-41 °/₀ of the hydrogen introduced in the halide (according to the experimental conditions), showed that considerable reaction between methylene and hydrogen occurred. Fig. 1B gives the plot of the logarithm of the ratio, CH_4/C_2H_4, against temperature at constant hydrogen pressure. The slope of the curve shows that the difference between the activation energies of the methane- and ethylene-forming reactions was 13·5 kcal. If, as before, we assume that the dimerisation of CH_2 radicals to form ethylene reaction has zero activation energy, then this value refers to the reaction producing methane. The magnitude of the activation energy is the same as in the corresponding reaction in nitrogen but the reaction mechanism is different. An additional reaction (9) consuming hydrogen and producing methane must also have taken place:

$$CH_2 + H_2 \longrightarrow CH_4 \quad . \quad . \quad . \quad . \quad (9)$$

The total carbon yield as CH_4 and C_2H_4 varied from 66-83 % of the methylene formed and the deficiency of carbon may be explained by the simultaneous occurrence of reaction (6). Increase in hydrogen pressure at constant temperature produced little change in the CH_4/C_2H_4 ratio, and thus it appears that the increased probability of recombination of methylene by triple-body collision was compensated by the increased tendency of reaction (9) at higher pressures. This view is supported by the fact that as the pressure of hydrogen was increased, the amount used up increased correspondingly. Rosenblum,[4] who photolysed ketene in the presence of hydrogen, observed the formation of about 1 % of methane at room temperature and 8 % at 200° C. He proposed the alternative reaction:

$$CH_2 + H_2 \longrightarrow CH_3 + H \quad . \quad . \quad . \quad . \quad (10$$

Reaction (10) is, however, endothermic to the extent of 19 kcal. and thus would require an activation of at least this amount. Furthermore, no ethane was formed in the reaction. The direct association reaction (9) is slightly exothermic and is thus the more probable reaction. It is therefore concluded that the reactions occurring were (5), (9) and (6), and that reaction (9) had an activation energy of 13·5 kcal.

Methyl Radicals.

It has usually been assumed that methyl radicals formed by thermal dissociation processes in an inert atmosphere readily dimerise to give ethane. It was, therefore, a somewhat unexpected result when we observed that methyl radicals formed from methyl iodide and excess atomic sodium in nitrogen at 300-363° gave methane in higher yields than ethane. A plot of the logarithm of the ratio of methane to ethane at a series of temperatures is shown in Fig. 2. The material balances showed that 80-85 % of the carbon of the methyl radicals produced was recovered as $CH_4 + C_2H_6$ and that very small amounts of ethylene and no other volatile hydrocarbons were formed. The hydrogen balance showed that almost all appeared in the $CH_4 + C_2H_6$, and thus the missing carbon was formed as free carbon, as with the methylene reactions.

The ethane was formed by the straightforward association reaction,

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad . \quad . \quad . \quad . \quad (11)$$

[4] Rosenblum, *J. Amer. Chem. Soc.*, 1938, 60, 2819 and *ibid.*, 1941, 63, 3322.

and since the relative amount of ethane increased with increase in nitrogen pressure at constant temperature, it appears that, at least in part, the ethane formation occurred in the gas phase and required a triple-body collision. The formation of methane must have occurred by a disproportionation reaction of the methyl radical and the most probable reaction is

$$CH_3 + CH_3 \longrightarrow CH_4 + CH_2 \quad . \quad . \quad . \quad (12)$$

The failure to observe ethylene in the products indicates that the methylene radicals did not dimerise but underwent further reaction. This must be so since the percentage of carbon introduced appearing as methane was about 60 %, whereas any disproportionation reaction of the above type could give only 50 % methane as a maximum value. Furthermore, the methane was not formed by reaction (6) since this process requires an activation energy of at least 14 kcal., whereas the activation energy of the methane-forming reaction in the present case was only 8 kcal. It

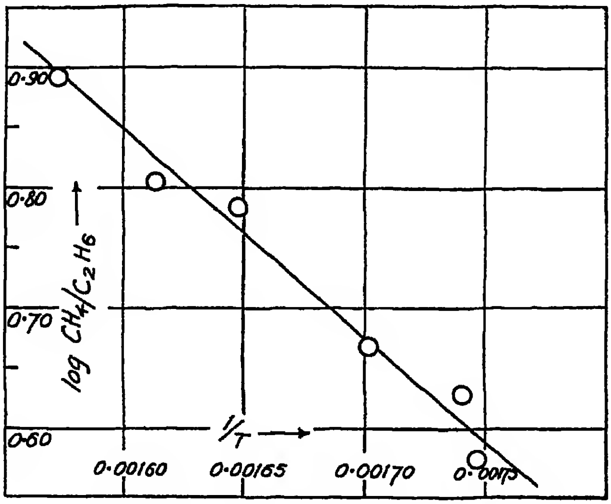

FIG. 2.—Methyl radicals in nitrogen. $p_{N_2} = 6{\cdot}4$ mm.

seems, therefore, that the succeeding stages of methane production were the reactions:

$$CH_3 + CH_2 \longrightarrow CH_4 + CH \quad . \quad . \quad . \quad (13)$$
$$CH_3 + CH \longrightarrow CH_4 + C. \quad . \quad . \quad . \quad (14)$$

These reactions must be relatively fast compared with

$$CH_2 + CH_2 \longrightarrow C_2H_4$$

in order to explain the absence of ethylene.

The energy for the removal of the first hydrogen in methane is 102 kcal. and that for the dissociation of the C—H molecule is 80 kcal. Long and Norrish [5] consider that the energy for the breaking of the C—H bond in the methyl radical is approximately that for removing the first hydrogen from methane. The C—H bond in CH_2 is certainly much weaker than this value. It follows, therefore, that whereas reaction (12) is approximately thermo-neutral, reactions (13) and (14) are 20 kcal. exothermic. Since these reactions, therefore, probably require a lower activation energy than (12) it is concluded that (12) was the rate-determining reaction for methane production. Assuming that the recombination of

[5] Long and Norrish, *Proc. Roy. Soc. A*, 1946, 187, 337.

methyl radicals requires no activation energy, the activation energy of 8·0 kcal. may be assigned to reaction (12).

It is not yet certain whether this reaction was heterogeneous or not. Increase in the surface/volume ratio of the reaction vessel by 1·6 produced only a slight change in the CH_4/C_2H_6 ratio under comparable experimental conditions. It is hoped to investigate this matter further in a modified apparatus.

Methyl Radicals in Hydrogen.—The plot of the logarithm of the methane/ethane ratio against temperature for the reaction of methyl in hydrogen for two reaction vessels is shown in Fig. 3. In the large vessel (5-l. capacity) the overall activation energy had a small negative value whilst in the smaller vessel it was not greater than +2 kcal. positive. Hence, taking the mean of these two sets of data, the ratio of the activation energies of the methane- and ethane-forming reactions was of the order of 1 ± 1 kcal. In contrast to the results in nitrogen,

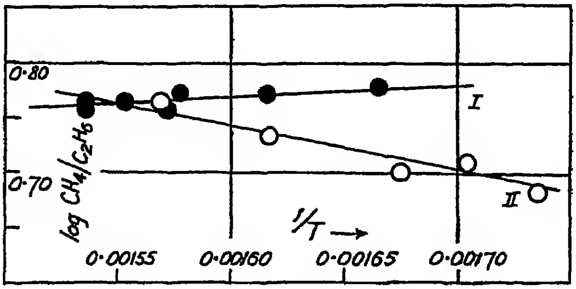

FIG. 3.—Methyl radicals in hydrogen. Curve I. Spherical vessel of radius 11 cm. and $p_{H_2} = 5·9$ mm. Curve II. Cylindrical vessel of radius 3·5 cm. and $p_{H_2} = 6·3$ mm.

all the carbon introduced as methyl radicals was recovered as $CH_4 + C_2H_6$. As before, the ethane was formed by the reaction

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

but the methane-producing reaction was in this case

$$CH_3 + H_2 \longrightarrow CH_4 + H \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The reaction

$$CH_3 + CH_3 \longrightarrow CH_4 + CH_2$$

found in nitrogen is now excluded, since not only does this reaction require 8 kcal. activation energy, but also the subsequent reaction of methylene, namely, $CH_2 + H_2 \longrightarrow CH_4$, has an activation energy of 13·5 kcal. The important reaction was therefore (16), and had an activation energy of about 1 kcal. This is considerably lower than the accepted value for this reaction, which is fairly well established as about 9 kcal. The result is, however, dependent on the assumption that the association reaction (15) has an activation energy of zero. Agreement with previous measurements would result if this reaction had an activation energy of 8 kcal. Since there is no evidence to support the latter view, and no suitable alternative to (16) may be suggested, we are forced to the conclusion that reaction (16) under these experimental conditions occurred as a surface reaction and, as the results in the next section indicate, it was probably catalysed by sodium atoms. Further work is in progress to decide this question.

Methyl Radicals in Excess Methyl Iodide in Hydrogen.—When the experimental conditions were reversed so that the methyl iodide was in excess and a normal diffusion flame was formed, the ratio of the methane/ethane production increased with temperature. The plot of the logarithm of this ratio against temperature is shown in Fig. 4 and the slope gives an activation energy of 8·8 kcal. The reactions taking place were precisely the same as those in excess sodium, viz. reactions (15) and (16), since independent investigations have shown that the reaction of methyl with methyl iodide, viz.:

$$CH_3 + CH_3I \longrightarrow CH_4 + CH_2I^- \quad . \quad . \quad . \quad (17)$$

required an activation energy of 13 kcal. and may thus be excluded. The measured activation energy of 8·8 kcal. may therefore be assigned to reaction

(16). This agrees with the results of Hartel and Polanyi [6] who used the same experimental procedure but followed the reaction by measurement of the hydrogen consumed rather than by analysis of the products. The abnormality of the corresponding reaction in the presence of a large excess of atomic sodium is not clear, but it does appear that sodium in some way behaves as a powerful reaction catalyst.

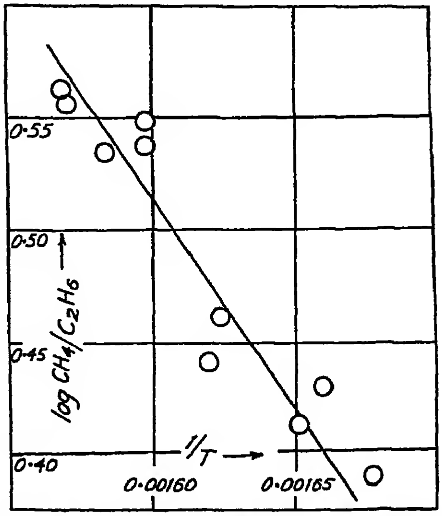

FIG. 4.—Methyl radicals in excess methyl iodide with hydrogen as carrier gas. $p_{H_2} = 5{\cdot}8$ mm.

Ethyl Radicals.

Ethyl radicals in nitrogen gave large percentage amounts of ethane and ethylene, together with the dimerisation product, butane. The results for a nitrogen pressure of 5·2 mm. are summarised in Table I.

It is seen that variations in temperature produced little change in the products, and the ratio of the ethane to butane yield was constant. The production of the three gases can be explained by assuming that the following two simple reactions occurred:

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \quad . \quad . \quad . \quad . \quad (18)$$
$$C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \quad . \quad . \quad . \quad (19)$$

The many other disproportionation reactions such as

$$C_2H_5 + C_2H_5 \longrightarrow C_3H_6 + CH_4 \text{ or } C_3H_8 + CH_2, \text{ etc.}$$

which may be postulated do not seem to have occurred.

TABLE I.—REACTION OF ETHYL IODIDE WITH EXCESS ATOMIC SODIUM IN NITROGEN, 5·2 mm. PRESSURE. (SODIUM PRESSURE = 10^{-3} mm.).

Moles of Carbon Introduced as $C_2H_5I \times 10^4$.	Temp. °C.	Per cent. Carbon Introduced appearing as:			Total Carbon Yield %.	Total Hydrogen Yield %.	Ratio by Volume C_2H_6/C_4H_{10}.
		C_2H_6.	C_2H_4.	C_4H_{10}.			
1·79	302	32·5	21·5	33	87	89	2·0
1·95	301	31·5	17·5	36·5	85·5	88·5	1·7
1·89	333	36·5	18	33	87·5	91	2·2
2·06	367	37·0	21·5	38	96·5	100	2·0
2·00	321	30·0	28	35	93	93	1·7
1·91	342	29·5	16·5	34·5	80·5	83	1·7
1·95	352	35	16·5	41	93·5	96·5	1·7
2·13	300	30·5	20·5	32·5	83·5	86	1·9

Reaction (19) should yield equal quantities of ethane and ethylene, but it is observed from Table I that the ethylene percentage was always lower than the ethane. This was probably due to a small amount of polymerisation of the ethylene, which occurs in the presence of sodium, and the ethylene so lost accounts approximately for the difference of the

[6] Hartel and Polanyi, *Z. physik. Chem. B*, 1930, 11, 97.

carbon yield from 100 %. The ratio of the ethane to butane yields may, therefore, be taken as a measure of the occurrence of reaction (19). Since this was independent of temperature the dimerisation and disproportionation reactions must have the same activation energy. If it is assumed that the association reaction of ethyl radicals has zero activation energy, then reaction (19) will occur without activation.

The low activation energy for the disproportionation reaction is in agreement with the observation that ethyl radicals from the dissociation of silver ethyl in alcohol readily undergo disproportionation at − 30° C.[7] The photolysis of ethyl iodide,[8] diethyl ketone,[9] and zinc and mercury diethyls [10] at temperatures of 25-45° C. produce ethyl radicals and the formation of ethane and ethylene in large amounts can be explained by the occurrence of the disproportionation reaction.

Ethyl Radicals in Hydrogen.—In hydrogen gas, ethyl radicals formed very little ethylene and thus the disproportionation reaction (19) was replaced mainly by the reaction between ethyl radicals and hydrogen:

$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H \quad . \quad . \quad . \quad . \quad (20)$$

The results at an average hydrogen pressure of 7 mm. are summarised in Table II. It is seen that the ratio C_2H_6/C_4H_{10} was independent of temperature and thus

TABLE II.—ETHYL RADICALS IN HYDROGEN. HYDROGEN PRESSURE, 7·0 mm. SODIUM PRESSURE = 10^{-3} mm.

Temperature °C.	Per cent. Carbon appearing as:			Total Carbon Yield %.	Ratio by Volume C_2H_6/C_4H_{10}.
	C_2H_6.	C_2H_4.	C_4H_{10}.		
303	40·5	3·5	40·0	84·0	2·0
316	38·5	4·0	46·5	89·0	1·7
331	38·5	4·0	51·0	93·5	1·5
346	35·5	6·0	52·5	94·0	1·4
304	36·5	4·0	49·0	89·5	1·5
361	44·0	6·0	42·0	92·0	2·1
324	42·5	4·5	45·5	92·5	1·9

the activation energy of reaction (20) is the same as that of radical recombination, $C_2H_5 + C_2H_5 \longrightarrow C_4H_{10}$.

One of us (C. F. H. T.) thanks the D.S.I.R. for a maintenance grant.

Summary.

Methylene, methyl and ethyl radicals formed homogeneously by the reaction of the corresponding halides with sodium atoms at 300-360° C. dimerise and disproportionate according to the following reaction scheme:

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad . \quad . \quad (1) \qquad C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \quad . \quad . \quad (5$$
$$CH_3 + CH_3 \longrightarrow CH_4 + CH_2 \quad (2) \qquad C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \quad (6$$
$$CH_3 + CH_2 \longrightarrow CH_4 + CH \quad (3) \qquad CH_2 + CH_2 \longrightarrow C_2H_4 \quad . \quad . \quad (7$$
$$CH_3 + CH \longrightarrow CH_4 + C \quad . \quad (4) \qquad CH_2 + CH_2 \longrightarrow CH_4 + C \quad . \quad (8$$

In hydrogen the primary reactions which occur, together with the dimerisation reactions (1), (5) and (7), have been shown to be

$$CH_2 + H_2 \longrightarrow CH_4$$
$$CH_3 + H_2 \longrightarrow CH_4 + H$$
$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H.$$

The activation energies of the disproportionation and hydrogen reactions have been determined.

[7] Bawn and Whitby, *Trans. Faraday Soc.*, this Discussion.
[8] West and Schlessinger, *J. Amer. Chem. Soc.*, 1938, 60, 961
[9] Ells and Noyes, *ibid.*, 1939, 61, 2492.
[10] Moore and Taylor, *J. Chem. Physics*, 1940, 8, 466.

Résumé.

Les radicaux méthylène, méthyle et éthyle, formés par réaction homogène des halogénures correspondants avec des atomes de Na à 300-360° c. se dimérisent et présentent une dismutation ; on suggère un schéma détaillé de réaction, en l'abscence ou en présence d'hydrogène. On a déterminé les énergies d'activation pour la dismutation et pour la réaction de l'hydrogène.

Zusammenfassung.

Methylen-, Methyl- und Äthylradikale, die bei der homogenen Reaktion der entsprechenden Haloide mit Na-Atomen bei 300-360° c. gebildet werden, dimerisieren und disproportionieren. Es wird ein ausführliches Reaktionsschema für sowohl Gegenwart als auch Abwesenheit von Wasserstoff vorgeschlagen. Die Aktivierungsenergien sind für die Disproportionierung und die Wasserstoffreaktionen bestimmt worden.

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LABILE MOLECULES IN THE KINETICS OF HYDROCARBON REACTIONS.

BY C. F. CULLIS, C. N. HINSHELWOOD, M. F. R. MULCAHY and R. G. PARTINGTON.

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PART I. INTRODUCTION.

BY C. N. HINSHELWOOD.

Two kinds of labile molecule appear in chemical kinetics : on the one hand, the activated complex molecule whose excess energy causes instability when the correct distribution is achieved : on the other hand, the free radical which in its turn exhibits two kinds of instability : (*a*) its tendency to saturate its valency by combining and (*b*) its susceptibility, in virtue of its unbalanced electronic structure, itself to suffer decomposition into smaller parts. Such internal decompositions of radicals play characteristic parts in the pyrolysis of ethers. Problems connected with these different kinds of instability are presented by the reactions of hydrocarbons in an interesting way.

One of the most remarkable characteristics of hydrocarbon oxidation is the very rapid increase in rate with the length of the carbon chain. This is shown in Fig. 1 which is based upon results discussed more fully in Part III. The marked dependence upon carbon chain length contrasts with what is found for the thermal decomposition, which is considered in Part II. There is, then, an effect peculiar to the oxidation reactions. This at once rules out the idea that the increased chain length facilitates reaction by adding to the number of internal degrees of freedom in which energy can be stored up, though the approximate constancy of rate of pyrolysis from C_4 upwards itself raises interesting questions.

The oxidation of hydrocarbons involves unstable intermediates in a rather remarkable way. The fundamental reason for this lies in the fact that oxygen is diatomic, while most of the oxidation products require the separation of the two oxygen atoms. The mode of their separation is evidently the key to the whole problem. An equation of the type :

$$CH_3 . CH_3 + O_2 = CH_3CHO + H_2O$$

tells us little since the changes of molecular pattern involved are too complex to have occurred except in stages. The whole trend of modern kinetic studies has been to show that the individual steps of reaction mechanisms usually involve few atomic movements and that these must be of the simplest character.

As is argued in detail in Part III, the only likely initiation of oxidation is by a series of simple changes leading from RH, the parent hydrocarbon, to a peroxide, R—O—O—R′ (where R′ may be R itself, or H). The general principle of minimum disturbance of existing structures takes us so far. The necessity for the separation of the oxygen atoms now comes into the picture. A very important character of oxygen suggests an answer. The single bond O—O is known to be much weaker than half the double bond O=O, the energy having been estimated to be as low as 35,000 cal.[1] The possibility, at moderate temperatures, of the direct resolution

$$\text{R—O—O—R}' = \text{R—O—} + \text{R}'\text{—O—}$$

must therefore be considered quite seriously. Here we have a labile molecule giving rise to branching chains but at a rate restrained by the magnitude of the activation energy necessary. This is, of course, precisely

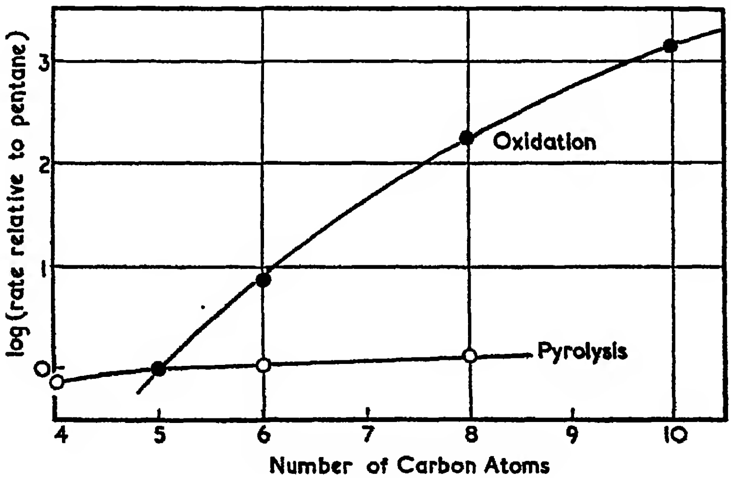


Fig. 1.

what is required by Semenov's general theory of slow chain-branching processes. Such a theory is required to explain many of the general features of oxidation reactions (Part III).

The probable behaviour of the alkoxyl radicals is of interest in relation to the question of stability. R—O— may be written $R'CH_2O$—. The decomposition of this into R′ and HCHO requires a simple shift of electrons:

$$\mathrm{R}'\!:\!\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}\!:\!\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\cdot \;=\; \mathrm{R}'\cdot \;+\; \underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}\!::\!\ddot{\mathrm{O}}\!:$$

and it is very tempting to believe that this is the source of the formaldehyde produced so readily in the earlier stages of oxidation even of long-chain hydrocarbons. Additional evidence on this HCHO production is described in Part III.

The pronounced effect of carbon chain length on oxidation rate would,

[1] Syrkin and Dyatkina, *Chemical Linkage and Molecular Structure* (Moscow, 1946), p. 305.

according to the views given above, depend upon variations in the stability of the peroxides. In this connection the first point to observe is that comparatively small changes in stability could have a considerable effect on the rate. This follows from the form of the kinetic equations. These lead to an expression for the oxidation rate, which is of the form :

$$\frac{f([O_2], [RH])}{1 - 2kF} \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the velocity constant of the key reaction involving the splitting of the O—O link, and F is a function of reactant concentrations and of various velocity constants. One of the conditions that the chain reaction should attain a high rate is that the denominator of this expression should become small, that is, that $2kF$ should not be too far removed from unity. Precisely in these circumstances relatively small changes in k can produce a greatly magnified effect on the rate.

This brings us to the important question of the influence of the nature of the hydrocarbon radical R on the tendency of the bond in R—O—O—R′ to break. Some guidance on what to expect is provided by an early paper of Burton and Ingold [2] who give reasons for believing that the stability of a neutral alkoxyl radical should be increased by electron-releasing groups. Hydrocarbon chains are well known to have electron-releasing properties which increase with the length of the chain. Thus increasing size of the hydrocarbon molecule will cause increases in k relative to other terms in the rate expression, and this increase may be magnified in the way explained.

In this way it might be possible to interpret the remarkable influence of hydrocarbon chain length on the oxidation. The influence of structure in another respect is not so simply dealt with. Oxidation is much more difficult with branched-chain hydrocarbons than with their straight-chain isomers (Part III), and once again, this contrast does not appear in the pyrolysis. The interpretation might depend upon some dynamical difference between the straight and the branched chains, and it must be said that there is room here for many possibilities, the understanding of the modes of vibration of such chains being at present extremely imperfectly understood. If this were so, however, one might expect some reflection of the difference to appear in the pyrolysis studies. Since it does not, one is tempted to suppose that the explanation lies rather in the magnitude and ease of transmission of electron-release effects to the oxygen bond which has to be severed.

Here again the principles of transmission are not fully understood. There is the well-known controversy about the nature of the influence exerted by tertiary alkyl groups; and the need for greater electron-release than is normally accounted for finds expression in the idea of hyperconjugation.[3] According to this idea CH_3 is written $H_3{\equiv}C{-}$ and the formal triple bond regarded as capable of participating in conjugation phenomena. If a straight chain is written $H_3{\equiv}C{-}\underset{\underset{H_2}{\|}}{C}{-}\underset{\underset{H_2}{\|}}{C}{-}$ it may be supposed capable of transmitting charge movements of the types

and some kind of coupled system of such changes might contribute to a momentary intense accumulation of negative charge on a terminal oxygen. When a normal chain is interrupted by branching there could be, conceivably, an impairment of the coupled vibrations and a diminished

[2] *Proc. Leeds Phil. Soc.*, 1929, 1, 421.

[3] Mulliken, Rieke and Brown, *J. Amer. Chem. Soc.*, 1941, 63, 41.

transmission, but too little seems to be known about such phenomena to reach a conclusion at the present moment. More experimental work seems to be needed.

Résumé.

On discute le rôle des molécules labiles dans les réactions des hydrocarbures, particulièrement en ce qui concerne l'accroissement rapide de la vitesse d'oxydation de ces composés en fonction de la longueur de la chaîne de carbone, en opposition avec la faible variation de la vitesse de pyrolyse avec le dimension et la complexité de la molécule après C_4.

Zusammenfassung.

Die Rolle, die labile Moleküle in den Reaktionen von Kohlenwasserstoffen spielen, wird mit besonderem Hinweis auf den Kontrast zwischem dem raschen Ansteigen der Oxydationsgeschwindigkeiten dieser Verbindungen mit anwachsender Länge der Kohlenstoffkette einerseits und der geringen Beeinflussung der Geschwindigkeit des thermalen Zerfalls durch Grösse und Komplexität des Moleküls nach C_4 andererseits besprochen.

PART II. THE RATES OF THERMAL DECOMPOSITION OF SATURATED HYDROCARBONS.

By R. G. Partington.

Received 17th June, 1947.

Many substances with complex molecules decompose at absolute rates which are great enough, even when chain reactions are inhibited, to suggest that the numerous internal degrees of freedom in a complex molecule can constitute or are convertible into activation energy. In this case the expression for the maximum possible rate becomes

$$k = \frac{\text{constant} \,.\, e^{-E/RT}(E/RT)^{\frac{1}{2}n-1}}{(\frac{1}{2}n - 1)\,!} \quad . \quad . \quad . \quad (I)$$

where n is the number of square terms associated with the internal degrees of freedom, k the rate constant and E the energy of activation.

The values for the energy of activation for the thermal decomposition of both ethane and n-hexane in the presence of nitric oxide (when reaction chains are inhibited) are approximately equal,

ethane . . .	74,500 cal.[1]
n-hexane . .	74,000 cal.[2]

and are slightly less than the approximate value for the bond strength, namely 80,000 cal./mol. Assuming that the value for the energy of activation for the chain-inhibited decomposition of all saturated hydrocarbons is approximately 74,000 cal./mol., the question arises whether their rates of decomposition might depend on the number of internal degrees of freedom, which will increase steadily with the length of the hydrocarbon chain and the complexity of the molecule.[3] Experiment has shown that this is not so.

Measurements have been made of the rates of decomposition of ethane, propane, butane, n-pentane, n-hexane, n-octane, 2-methyl-pentane, 3-methyl-pentane, 2 : 3-dimethyl pentane and 2 : 2 : 4-trimethyl pentane under identical conditions, and it was found that after propane, the rate of decomposition was almost independent of the size or shape of the molecule.

[1] Staveley, *Proc. Roy. Soc., A*, 1937, **162**, 557.
[2] Partington (unpublished result).
[3] Cf. discussion of Burk, *J. Physic. Chem.*, 1931, **35**, 2446.

Experimental and Results.

The hydrocarbons were decomposed in a silica bulb heated in an electric furnace. The temperature of the reaction vessel was measured with a Pt/Pt-Rh thermocouple and was controlled by the appropriate adjustment of the E.M.F. applied to the furnace windings. The decompositions were carried out at constant volume; the pressure in the reaction vessel was measured with a mercury manometer. The gaseous hydrocarbons were stored in a glass bulb, and in order to introduce those that were liquid at room temperature, the small bulb in which they were stored was heated by immersion in a beaker of hot water. The nitrometer in which the nitric oxide was prepared (by the action of mercury on concentrated nitric acid in the presence of excess concentrated sulphuric acid) was sealed into the apparatus. With the exception of the reaction vessel, the apparatus was made of soda-glass and could be evacuated by means of a mercury diffusion pump backed by a rotary oil pump. The initial rate of decomposition was measured by the rate of increase of pressure with time at zero increase of pressure, readings being taken of the manometer level at convenient intervals of time. These were plotted, and the exact initial pressures and rates were obtained from the graph by extrapolation and tangent estimation respectively. The lead-in tubes and the manometer were wound with thin Nichrome wire and heated electrically to prevent condensation. For each hydrocarbon, r_0 the initial rate was measured for a series of different initial pressures (p_0) from 50 to 150 mm. These values were plotted and k was taken as $(dr_0/dp_0)_{p_0 = 100\text{ mm.}}$ All the measurements were made at 530° C. The results are given in the Table.

TABLE.

k (min.$^{-1}$) for thermal decomposition at 530° C.

Hydrocarbon.	$k_1 \times 10^3$ (without NO).	$k_2 \times 10^3$ (with 5 mm. NO).
Ethane	4·0	0·07
Propane	18	2·4
n-Butane	45	18
n-Pentane	100	24
n-Hexane	100	25
n-Octane	100	35
2-Me-pentane	60	30
2:3-di-Me-pentane	160	120
2:2:4-tri-Me-pentane	170	100

The results are represented diagrammatically in Fig. 1.

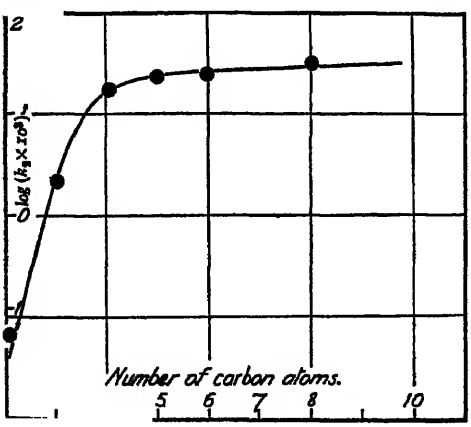


FIG. 1.

Discussion.

According to the expression (I), d ln k/dT

$$= \frac{E - (\frac{1}{2}n - 1)RT}{RT^2}.$$

Thus the value for E_A obtained from the gradient of the (ln k) — $1/T$ plot must be corrected, the true value being

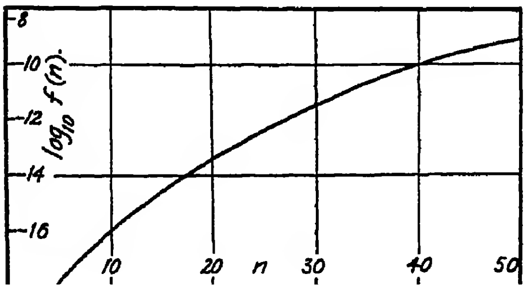
$$E_A + (\tfrac{1}{2}n - 1)RT.$$

The expression for the maximum possible rate thus becomes

$$\text{const.}\ \frac{e^{-\{E_A + (\frac{1}{2}n - 1)RT\}/RT} \cdot \left\{\frac{E_A + (\frac{1}{2}n - 1)RT}{RT}\right\}^{\frac{1}{2}n-1}}{(\frac{1}{2}n - 1)\,!} = \text{const. f}(n).$$

E_A is taken as 74,000 cal., $R = 1·98$ and $T = 803°$ K. Values of f(n) are plotted against n in Fig. 2.

The value of n for the molecules studied is not known, but it does not seem probable that there is any connection between the course of the curves in Fig. 1 and 2. With very large values of n the curves in Fig. 2 must flatten, but the values where this would occur seem to be in any case improbably large. What seems possible is that in the large molecules there is very incomplete sharing of energy between bonds, so that these molecules behave as if they consisted of a limited number of virtually rigid parts between which the interchange of energy does not count for the purposes of chemical reaction. But in any case, maximum possible rate and actual rate need not be directly related. A fuller explanation may be possible when the work in progress on the analysis of the initial decomposition products has been completed. In the meantime the principal object of this paper is to emphasise the insensitiveness of decomposition rate to chain length, in sharp contrast with what is found for the oxidation rates of hydrocarbons.



This work is part of the programme of the Fuel Research Board and is published with the approval of the Director of Fuel Research.

Summary.

The rates of thermal decomposition of ethane, propane, n-butane, n-pentane, n-hexane, n-octane, 2-methyl-pentane, 2:3-dimethyl pentane, 2:2:4-trimethyl pentane have been measured at 530° c. in the presence of sufficient nitric oxide to inhibit the chain reactions. The values show that after C_4, the rate is little dependent on the size or complexity of the molecule. According to the theory that the energy of vibrational degrees of freedom can contribute to the activation energy, the rate might increase rapidly with size and complexity of the molecule but such an effect is not in evidence.

Résumé.

La vitesse de décomposition par la chaleur a été mesurée pour les corps suivants: éthane, propane, n-butane, n-pentane, n-hexane, n-octane, méthyl-2-pentane, diméthyl 2 : 3 pentane et triméthyl-2-2-3 pentane, à 530° c. en présence de NO en quantité suffisante pour inhiber les réactions en chaîne. Après C_4, la vitesse ne dépend que faiblement de la dimension et de la complexité de la molécule.

Zusammenfassung.

Die Geschwindigkeiten des thermalen Zerfalls von Äthan, Propan, n-Butan, n-Pentan, n-Hexan, n-Oktan, 2-Methylpentan, 2, 3-Dimethylpentan und 2, 2, 4, Trimethylpentan sind bei 530° c. in Gegenwart von genügend NO um Kettenreaktionen zu unterdrücken gemessen worden. Nach C_4 wird die Geschwindigkeit nur wenig von der Grösse und Komplexität der Moleküle beeinflüsst.

PART III. LOW-TEMPERATURE OXIDATION OF HIGHER PARAFFINS IN RELATION TO STRUCTURE.

BY C. F. CULLIS AND C. N. HINSHELWOOD.

Received 17th June, 1947.

The experimental evidence on the subject of hydrocarbon oxidation is complex and the theoretical discussion confusing. The reason lies largely in the fact that different hydrocarbons have been studied by different workers under conditions not easily comparable. The aim of the present work is to make some comparative observations on a series of paraffins, and to attempt to account for the salient general facts by a theory rendered as manageable as possible by suitable approximations. This theory is essentially a form of Semenov's slow chain-branching theory.[1]

Certain workers have supposed thermal decomposition to precede oxidation.[2] The hydroxylation theory [3] on the other hand involves the disruption of an oxygen molecule. Callendar [4] assumed a binary reaction of hydrocarbon and oxygen to give a peroxide, and others have postulated an initial complex which is stabilised by isomerisation to a peroxide of the normal type.[5] Peroxides are detectable in combustion and, when added to paraffin-oxygen mixtures, act as catalysts for the oxidation. Egerton suggested that the peroxides initiate the chain reaction which is generally accepted to occur.[6]

A comprehensive theory must take into account the fact that the slow oxidation can apparently occur by two mechanisms. This was suggested by the negative temperature coefficient of the oxidation rate observed in a certain temperature range, usually around 350° C.[7, 8] It is probably due to the instability of intermediate products in the low temperature mode of oxidation.[9] Since the rate increases again from about 450° there is probably another mechanism which operates only to a small extent in the range where the low temperature mode prevails. The existence of two mechanisms may explain why the oxidation of methane or ethane differs rather markedly from that of the higher paraffins.[10, 11] No peroxidic substances are found in the oxidation of methane,[12] and those detected during the oxidation of ethane are probably only aldehyde peroxides.[13] No region of negative temperature coefficient is found with

[1] Semenov, *Chemical Kinetics and Chain Reactions* (Oxford, 1935).

[2] Lewis, *J. Chem. Soc.*, 1927, 1555; 1929, 759; 1930, 58. Berl, Heise and Winnacker, *Z. physik. Chem. A*, 1928, **139**, 453. Rice, *Ind. Eng. Chem.*, 1934, **26**, 259.

[3] Bone, *Proc. Roy. Soc. A*, 1932, **137**, 243.

[4] Callendar, *Aer. Res. Comm. Mem.*, 1926, 1062.

[5] Grün, *Ber.*, 1920, **53**, 987; Brunner and Rideal, *J. Chem. Soc.*, 1928, 1162.

[6] Egerton, *Nature*, 1928, **121**, 10.

[7] Pease, *J. Amer. Chem. Soc.*, 1929, **51**, 1839.

[8] Townend, *Chem. Rev.*, 1937, **21**, 259.

[9] Lewis and von Elbe, 1938, *Combustion, Flame and Explosions of Gases* (Cambridge).

[10] Prettre, *Bull. Soc. Chim.*, 1932, **51**, 1132; *Acta Physicochim.*, 1938, **9**, 581.

[11] Bone and Hill, *Proc. Roy. Soc., A*, 1930, **129**, 434; Bone and Allum, *ibid.*, 1932, **134**, 578; Pidgeon and Egerton, *J. Chem. Soc.*, 1932, 661; Norrish and Foord, *Proc. Roy. Soc., A*, 1936, **157**, 503; Harris and Egerton, *Chem. Rev.*, 1937, **21**, 287; Norrish and Wallace, *Proc. Roy. Soc. A*, 1934, **145**, 307; Kane, *ibid.*, 1939, **171**, 251.

[12] Prettre, *Acta Physicochim.*, 1938, **9**, 581; Norrish, *Proc. Roy. Soc. A*, 1935, **150**, 36.

[13] Bone and Hill, *loc. cit.*

the two simplest paraffins.[14] In the present work attention has been confined to the low temperature mode of oxidation of the paraffins from pentane upwards.

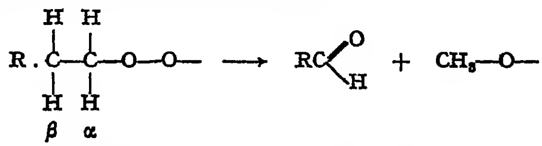
More detailed theories of hydrocarbon combustion applicable to the higher paraffins are those of Ubbelohde [15] and of Lewis and von Elbe.[9] A difficulty in most of the theories is the unlikelihood of some of the individual reaction steps postulated. Chemical reactions are now realised to occur in stages, each of which is usually accompanied by a minimum of disturbance of existing atomic configurations. The reaction

$$R . CH_3 + O_2 = RCH_2 . OOH$$

is sometimes written for the initiating process, but a more satisfactory assumption is that the formation of peroxide occurs in steps:

$$RCH_3 + O_2 = RCH_2^- + HO_2 ; \quad RCH_2^- + O_2 = RCH_2 . OO— ;$$
$$RCH_2OO— + RCH_3 = RCH_2OOH + RCH_2^-,$$

each of which involves the formation or disruption of only one bond. Another reaction which appears improbable is that sometimes written for the breakdown of peroxidic radicals:



This involves simultaneously the transference of a hydrogen atom from the β- to the α-carbon atom and the attachment of one of the oxygen atoms to the β-carbon atom.

The reaction $RCH_2 . C{<}^{O} + O_2 = R . C{<}^{O} + H_2O + CO$ also seems somewhat unlikely, depending upon the simultaneous abstraction of two hydrogen atoms by an oxygen atom and the attachment of the other oxygen atom to the carbon, together with the breaking of the linkage in the oxygen molecule and the splitting of the C—C bond to give CO. In the present discussion the principle has been followed that only reactions of the simplest type are admissible.

Even comparatively simple mechanisms for chain reactions can lead to highly complex rate expressions with many arbitrary constants. The oxidation of the higher paraffins is evidently of great complexity. What is therefore of importance is to formulate a simplified mechanism which shall do justice in a general way to the widest range of characteristic facts, even if numerical agreements are not more than semi-quantitative. Some of the broad facts are extremely striking and act as good pointers to the general form of theory to be constructed.

Among the striking features of the reactions are the following: (1) the remarkable influence of molecular structure of the hydrocarbon; (2) the existence of the induction period and the slow rise of the rate to a maximum; (3) the great effect of hydrocarbon pressure on the rate, and, in contrast, the fact that increase of oxygen pressure over wide ranges does not increase the rate, the influence of oxygen as a reactant being evidently counteracted by some actual retarding action; (4) the sensitivity of the reaction rate to the condition of the surface; (5) the formation of numerous intermediate products, including aldehydes, peroxides and acids, the concentrations of the two former running parallel with the oxidation rate; and (6) the specific effect of various inhibitors and accelerators, such as aldehydes.

[14] Townend and Chamberlain, *Proc. Roy. Soc. A*, 1936, 154, 95.
[15] Ubbelohde, *ibid.*, 1935, 152, 354.

Experimental.

The apparatus resembled that used in previous work in this laboratory. The reaction vessel was of silica (9 cm. long, 6·9 cm. diam.). The course of the reaction was followed by pressure-time records and by periodic analyses for specific intermediate products.

Peroxides were estimated iodometrically. Acyl and alkyl peroxides could be distinguished by the fact that only the former liberate iodine from neutral solutions of KI.[16] Addition of ferrous and molybdate ions as catalysts was used to help the decomposition of dialkyl and alkyl hydrogen peroxides.[17]

The total *aldehyde* concentration was determined by Ripper's bisulphite method.[18] The colorimetric method described by Ubbelohde, Drinkwater and Egerton [19] was not used since the colour was found to depend on the nature of the aldehyde, but the method given by the same authors for *formaldehyde* was adopted. It depends upon the fact that only formaldehyde restores the colour to a strongly acidified Schiff's reagent. Carboxylic acids were determined by titration with alkali with phenolphthalein as indicator.

Effect of Structure on Ease of Oxidation of Paraffins.

(*a*) STRAIGHT-CHAIN PARAFFINS.—The criterion of ease of oxidation was the maximum rate of reaction, attained after the end of the induction period, and

TABLE I.—INFLUENCE OF CARBON CHAIN LENGTH ON OXIDATION RATE.

Pressure of oxygen 250 mm. throughout.

Temp. (°c.).	Hydrocarbon. mm.	Max. Rate (mm./min.).	Ratio.	Rate Relative to Pentane (Approx.).	Number of Carbon Atoms.
202	pentane, 30	0·069	7·5	1	5
	hexane, 30	0·500		7·5	6
183	hexane, 30	0·059	26·6		
	octane, 30	1·57		200	8
186	octane, 8	0·123	6·9		
	decane, 8	0·85		1380	10

measured by the pressure-time records. The compounds investigated were *n*-pentane, *n*-hexane, *n*-octane and *n*-decane. The large differences between consecutive members of the series made it necessary to compare the compounds in pairs at different temperatures, since under conditions where one paraffin oxidised explosively, another failed to react at a measurable speed. This necessity introduces some uncertainty into the quantitative significance of the results, but the general trend is too marked to allow of any doubt about the order of magnitude of the effect. As far as possible the comparisons are made with equal pressures, though with *n*-decane and octane the measurements had to be made at somewhat lower pressures. The experimental results are shown in Table I.

(*b*) BRANCHED-CHAIN PARAFFINS.—In general branched-chain paraffins [20] oxidise less rapidly than corresponding straight-chain hydrocarbons. Once

[16] Clover and Houghton, *Amer. Chem. J.*, 1904, **32**, 43; Newitt and Baxt, *J. Chem. Soc.*, 1939, 1711.

[17] Ubbelohde and Egerton, *Phil. Trans. Roy. Soc. A*, 1935, **234**, 487.

[18] Ripper, *Sitzungsber. Akad. Wiss. Wien*, 1900, **109** (II*b*), 844.

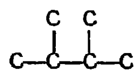
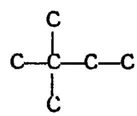
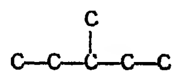
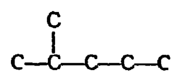
[19] Ubbelohde, Drinkwater and Egerton, *Proc. Roy. Soc. A*, 1935, **153**, 103.

[20] Pope, Dykstra and Edgar, *J. Amer. Chem. Soc.*, 1929, **51**, 2203.

again the comparisons had to be made, in bracketted pairs, at different temperatures, because of the enormous differences in reactivity. The results for various isomeric hexanes are given in Table II. The important fact which emerges from these measurements is that the ease of oxidation depends upon the length of the unbranched carbon chain in the molecule. This result is parallel with what is found in regard to the "knock" tendency of certain paraffinic fuels.[31] The impossibility of carrying out all the measurements under strictly comparable conditions lessens the quantitative significance of the results in Table II, but there is little doubt about the order of magnitude and the general nature of the effect.

TABLE II.—INFLUENCE OF STRUCTURE ON OXIDATION RATE OF ISOMERIC HEXANES.

Pressure of hydrocarbon 50 mm.; pressure of oxygen 200 mm.

Temp. (°C.).	Hydrocarbon.	Max. Rate (mm./min.).	Ratio.	Approx. Ratio Relative to 2:3-Dimethyl butane.	Structure.
264	2 : 3-dimethyl butane	0·550	12	1	
	2 : 2-dimethyl butane	6·63		12	
250	2 : 2-dimethyl butane	0·62	5		
	3-methyl pentane	3·10		60	
227	3-methyl pentane	0·243	9·3		
	2-methyl pentane	2·25		560	
202	2-methyl pentane	0·455	2·8		
	n-hexane	1·25		1580	C—C—C—C—C—C

In respect of the structural influence the contrast between oxidation and pyrolysis is remarkable. To understand it further the various steps in the kinetics need more detailed scrutiny.

The Induction Period.

The criterion used in this work as a measure of the induction period has been the time elapsing between the admission of the oxygen to the hydrocarbon in the reaction vessel and the occurrence of a given very small pressure change (normally 2 mm.). After this point the reaction accelerates rapidly to its maximum rate. Some preliminary experiments were made with

[31] See Lovell and Campbell, *Chem. Rev.*, 1938, **22**, 159.

a sample of "spectroscopically pure" hexane (that is free from aromatic hydrocarbons but not otherwise specially pure). The oxidation proceeded at a convenient rate at 227° and the induction period was of the order of 5 min. It was strongly dependent on the concentration both of oxygen and of hydrocarbon, slightly shortened by added nitrogen and independent of pre-heating of the hydrocarbon. Chemical analysis for possible intermediates indicated that no appreciable quantities of these substances were formed during the induction period, their formation only becoming apparent after the pressure had begun to rise.

Experiments were then made under comparable conditions with very pure hexane, which oxidised at a very much greater rate. At 202° and 250 mm., for example, the induction periods for 1 : 4-hydrocarbon-oxygen mixtures were 3·5 min. and 30 min. for the pure compound and the "spectroscopically pure" substance respectively. Once again the induction period decreased with increasing pressure either of hexane or of oxygen. An important distinction between the pure and impure hydrocarbons was found in the fact that in the oxidation of the former detectable amounts of peroxides, aldehydes and acids began to accumulate from the beginning. Pre-heating of the hydrocarbon again had no effect. Similar results were found with *n*-pentane. With *n*-octane a definite pressure decrease occurs on the first admission of the gases to the reaction vessel : after 4 to 5 min. this is followed by the normal pressure increase.

There seem, then, to be two kinds of induction period : (*a*) a period of complete quiescence due to impurities and (*b*) a simple autocatalytic development of the reaction to maximum intensity. The reciprocal of the time in (*b*) is approximately linearly proportional to oxygen and hydrocarbon pressure (Fig. 1*a* and 1*b*).

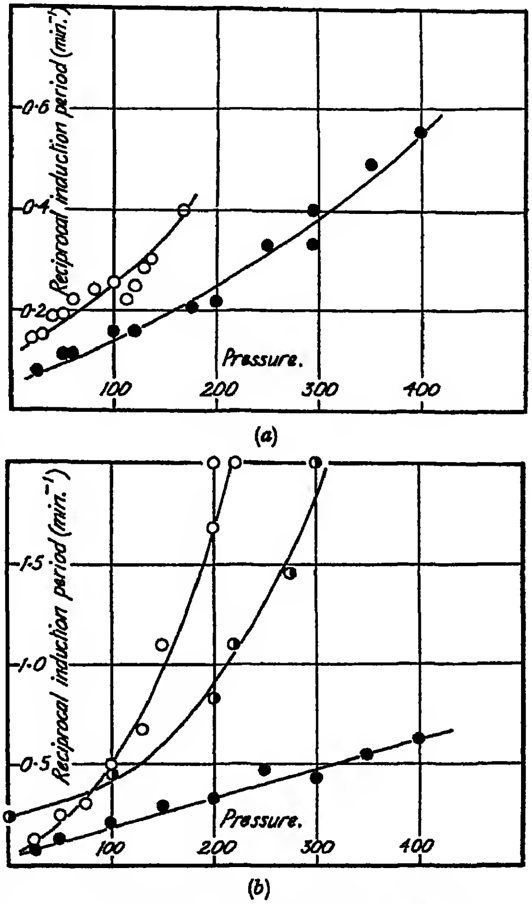


FIG. 1.—The variation of the induction period with the pressure of the reacting gases.

(*a*).—*n*-hexane. 202° C.
Open circles : hexane varied, oxygen = 100 mm.
Full circles : oxygen varied, hexane = 50 mm.

(*b*).—*n*-pentane. 227° C.
Open circles : pentane varied, oxygen 100 mm.
Full circles : oxygen varied, pentane 50 mm.
Half-filled circles : oxygen 200 mm., pentane 50 mm., nitrogen varied.

Influence of Hydrocarbon Concentration.—The maximum rate of reaction increases rather rapidly with increase of pentane or hexane concentration, the apparent order of reaction being between one and two (Fig. 2). The range of pressure over which measurements can be made is, however, restricted by the vapour pressure of the hydrocarbons.

Influence of Oxygen Concentration.—Over a wide range of oxygen pressures the rate of reaction is nearly independent of the oxygen pressure. Comparative results for pentane and hexane are shown in Fig. 2. The contrast in influence between oxygen and hydrocarbon is extremely significant.

Influence of an Added Inert Gas.—Addition of nitrogen to a pentane-oxygen mixture of fixed composition was found to have relatively little effect on the maximum rate of reaction, though, as already stated, the induction period was shortened (Table III).

Influence of the Surface.—When a vessel filled with silica tubes was substituted for the unpacked vessel described earlier, the induction period was lengthened and the rate of oxidation was even more markedly reduced. The results became erratic so that an accurate quantitative comparison could not be made. The matter is to be investigated further.

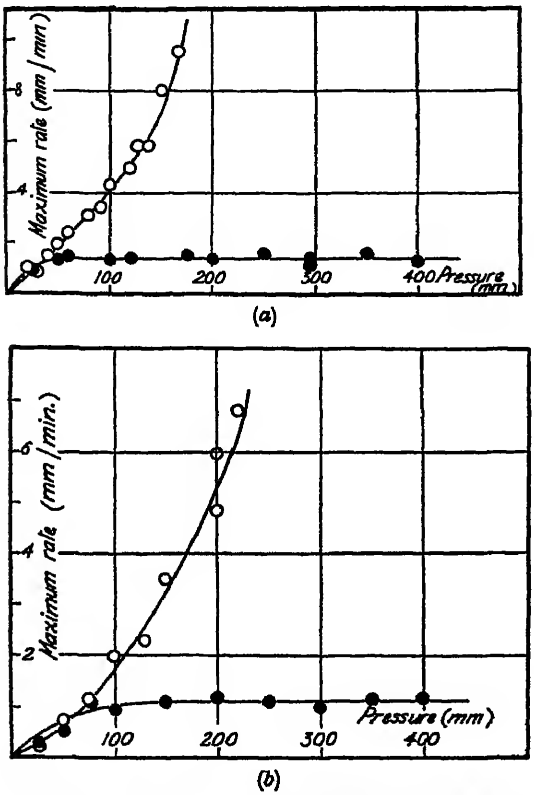


FIG. 2.—The variation of the maximum oxidation rate with the pressure of the reacting gases.

(*a*).—*n* hexane. 202° C.
Open circles : hexane varied, oxygen 100 mm.
Full circles : oxygen varied, pentane 50 mm.

(*b*).—*n*-pentane. 227° C.
Open circles : pentane varied, oxygen 100 mm.
Full circles : oxygen varied, pentane 50 mm.

Analytical Results.

Some typical measurements are shown in Fig. 3. There is a close parallelism between the rate of reaction and the concentration of peroxide at any stage.[12] Alkyl peroxides and aldehyde peroxides contribute to the total peroxide concentration to a comparable extent. The aldehyde concentration passes through a maximum in much the same way as the peroxide though appreciable amounts remain at the apparent end of the reaction. The acids, however, increase continuously.

Higher aldehydes and formaldehyde appear in approximately equivalent amounts. The ratio, total aldehyde/HCHO, was investigated in some detail (Fig. 4), for various hexane-oxygen mixtures. Initially the ratio always tends to a value of about 2, one molecule of HCHO being formed for each molecule of higher aldehyde. The early appearance of the formaldehyde, *even at high hydrocarbon-oxygen ratios*, suggests that it is not produced by complete degradation of a C_2 chain, but is *split off from some labile intermediate*. The obvious source is a radical RCH_2O—.

[12] Cf. the cases quoted by Medvedev, *Acta Physicochim.*, 1938, 9, 395.

Inhibitors and Accelerators.

(*a*) Higher Aldehydes.—Addition of small amounts of CH_3CHO to pure hexane-oxygen mixtures revealed no catalytic effect. The aldehyde was found to oxidise more or less independently of the hydrocarbon. Similar results were found with propionic aldehyde, and with pentane in place of hexane. For this reason the aldehydes have not been assigned any key role in the oxidation of the hydrocarbon.

With the impure "spectroscopic" hexane, acetaldehyde eliminated the induction period and caused inflammation at temperatures where the rate would normally have been quite slow.

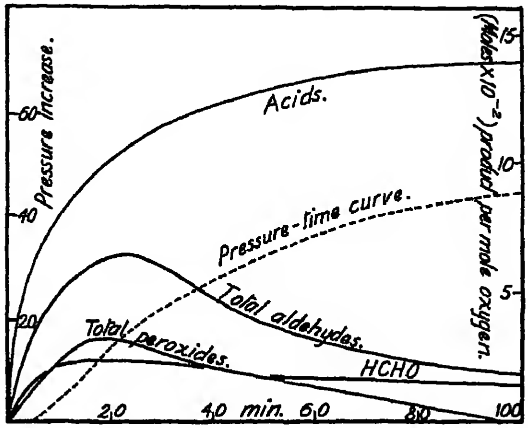


Fig. 3.—Analysis of products from oxidation of *n*-hexane at 202° C. Hexane 50 mm., oxygen 200 mm.

(*b*) Formaldehyde.—Moderate amounts of HCHO exert a powerful inhibitory effect and increase the length of the induction period very markedly. This is observed with pentane and with the pure and the impure hexane. Some typical results are shown in Table IV. Attempts were made to determine by analysis the fate of the HCHO. With the "spectroscopic" hexane it is destroyed at a steady rate and is practically consumed by the end of the induction period. With the pure *n*-hexane the concentration of HCHO remains constant during the induction period, the aldehyde being apparently destroyed and formed at equal rates. Control experiments showed that HCHO is not attacked by hexane or by oxygen alone under the conditions of the experiment, so that it must react with some intermediate formed from the hydrocarbon and the oxygen.

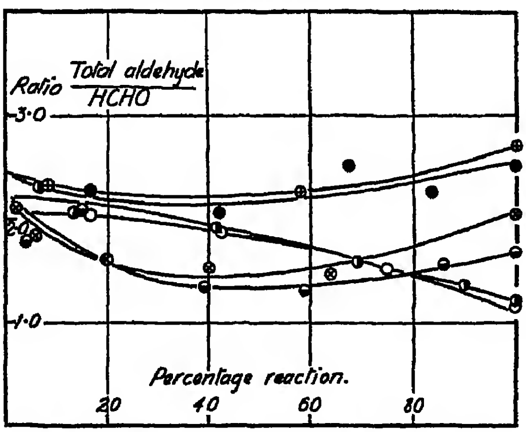


Fig. 4.—Variation of ratio, total aldehyde/HCHO, during reaction of hexane-oxygen mixtures at 202° C. Hexane/O_2 ratio: vertical crosses 10/1, black circles 4/1, horizontally divided circles 1/1, transverse crosses 1/4, open circles 1/8, vertically divided circles 1/12.

(*c*) Alcohols.—Neither *n*-hexyl nor *n*-propyl alcohol had any appreciable effect on the oxidation of *n*-hexane.

(*d*) Isomeric Paraffins.—The "spectroscopically pure" hexane evidently contains a powerful inhibitor which must be destroyed before oxidation can proceed. Its nature has not so far been discovered. Spectroscopic examination (for which we are indebted to Dr. Whiffen and Mr. Partington) showed the presence of 2-methyl and 3-methyl pentane and of an unidentified compound. Tests with the two isomers showed them not to be responsible for the inhibition.

In general it was found that a branched-chain paraffin does not inhibit the oxidation of the straight-chain isomer except when the two substances are present in comparable quantities. The reverse, however, is not true. For example, small amounts of *n*-hexane markedly accelerate the oxidation of 3-methyl pentane, as shown by the results in Fig. 5.

TABLE III.—VARIATION OF MAXIMUM RATE WITH PRESSURE OF ADDED NITROGEN.

Temperature 227° C. *n*-Pentane, 50 mm.; oxygen 200 mm.

Pressure of N_2.	Maximum Rate (mm./min.).
0	0·85
100	0·81
200	0·70
220	0·84
275	0·95
300	0·74

TABLE IV.—INFLUENCE OF FORMALDEHYDE ON THE INDUCTION PERIOD OF "SPECTROSCOPICALLY PURE" HEXANE

Hexane 50 mm.; oxygen 200 mm. Temperature 225° C.

HCHO (mm.).	Induction Period (min.).
0	18, 20, 12
0·25	17
0·4	15
1·5	40, 60
3·0	120
5·0	> 180
6·0	> 180

Discussion.

Two of the most characteristic facts about the oxidation reaction are, on the one hand, the "slow chain-branching" phenomenon, and, on the other, the remarkable influence of structure. It is natural to attempt to relate them. The essential hypothesis of the discussion will be that the chain branching is associated with the decomposition of peroxides, and that the stability of these labile molecules varies considerably with the nature of the hydrocarbon. The peroxides give alkoxyl radicals from which the formaldehyde readily splits off.

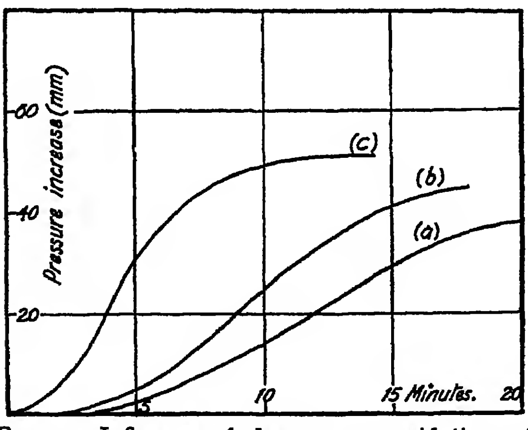


FIG. 5.—Influence of hexane on oxidation of 3-methyl pentane at 251° C. 3-methyl pentane 50 mm., oxygen 200 mm., hexane (*a*) 0, (*b*) 2·5 mm., (*c*) 5·0 mm.

The initiation is assumed to depend upon

$$RH = R + H \qquad (1a)$$

or

$$RH + O_2 = R + HO_2, \qquad (1b)$$

the rate being ϕ.

The radicals react as follows:

$$R + O_2 = R{-}O{-}O{-} \qquad (2)$$

$$R{-}O{-}O{-} + RH = R{-}O{-}O{-}R \qquad (3)$$

$$R{-}O{-}O{-} + RH = \text{relatively inactive products.} \qquad (4)$$

R—O—O— radicals react with more RH to give peroxides of which one is assumed to be of predominant importance, or at any rate representative

of all the active species and written simply ROOR.* The alternative reactions giving much less active bodies are schematised by (4).

The active bodies suffer two kinds of fate, a branching reaction:

$$\text{R—O—O—R} = 2\text{R—O—} \quad . \quad . \quad . \quad (5)$$

and a non-chain degradation:

$$\text{R—O—O—R} = \text{inactive products.} \quad . \quad . \quad . \quad (6)$$

R—O— may be written $R'CH_2O$— which will suffer the degradation:

$$R'CH_2O\text{—} = R' + CH_2O. \quad . \quad . \quad . \quad (7)$$

If (7) is assumed to follow directly on (5), the two are equivalent to

$$\text{R—O—O—R} = 2R' + 2\ CH_2O.$$

R′ may then react with RH regenerating R:

$$R' + RH = R + R'H \quad . \quad . \quad . \quad . \quad (8)$$

or with oxygen, entering a cycle of changes whereby a new radical R″ of still lower carbon content is ultimately formed

$$R' + O_2 = \text{less active products.} \quad . \quad . \quad . \quad (9)$$

To simplify the scheme, which with the higher hydrocarbons would otherwise present formidable complications, we make use of the key experimental fact that the rate of oxidation does actually decrease very markedly with diminishing number of carbon atoms. From this we infer that the regeneration reaction (8) will maintain the rate, while the degradation reaction (9) leads to forms of peroxide which are much less ready to maintain the branching reactions of type (5). As an approximation, therefore, (9) may be taken as a chain-breaking reaction. The inhibitory action of HCHO can be attributed to a reaction with R, but will not be taken into account in the following treatment (which will deal with the reaction in the absence of considerable amounts of products).

From the above equations we have:

$$d[R]/dt = \phi - k_2[R][O_2] + k_8[R'][RH] = 0$$
$$d[R']/dt = 2k_5y - k_8[R'][RH] - k_9[R'][O_2] = 0$$

where y represents [ROOR].

$$d[\text{R—O—O—}]/dt = k_2[R][O_2] - (k_3 + k_4)[\text{R—O—O—}][RH] = 0$$
$$dy/dt = k_3[\text{R—O—O—}][RH] - (k_5 + k_6)y$$

which must not be equated to zero since the active peroxide accumulates slowly.

Solving for y we obtain

$$y = \frac{k_3/(k_3 + k_4)\phi(1 - e^{-At})}{(k_5 + k_6) - \dfrac{2k_3}{(k_3 + k_4)} \cdot \dfrac{k_5k_8[RH]}{(k_8[RH] + k_9[O_2])}}$$

where A is an abbreviation for the denominator of this expression.

$$-d[O_2]/dt = k_2[R][O_2] + k_9(R')[O_2] = 2k_5 \,.\, y$$

$$= \frac{2\left(\dfrac{k_3}{k_3 + k_4}\right)\left(\dfrac{k_5}{k_5 + k_6}\right)\phi(1 - e^{-At})}{1 - 2\left(\dfrac{k_3}{k_3 + k_4}\right)\left(\dfrac{k_5}{k_5 + k_6}\right)\dfrac{k_8[RH]}{(k_8[RH] + k_9[O_2])}}.$$

* The formation of ROOH rather than ROOR would involve the reactions:

$$\text{R—O—O—} + RH = ROOH + R$$
$$\text{R—O—O—H} = \text{RO—} + OH = R' + HCHO + OH$$
$$OH + RH = R + H_2O,$$

a scheme which, kinetically, will not differ much from the sum of reactions 3, 5 and 8. Chain *branching* is again governed by the breakdown of the peroxide molecules.

This rate rises to a maximum before any serious consumption of reactants occurs, so that we may write:

$$p_{\text{max.}} = \frac{\text{constant } \phi}{1 - \dfrac{C_2[\text{RH}]}{[\text{O}_2] + C_3[\text{RH}]}} \quad . \quad . \quad . \quad (1)$$

where $[O_2]$ and [RH] are the initial concentrations, and C_2 and C_3 are constants.

We may now consider briefly how far this expression does justice to the characteristic facts.

(1) Molecular Structure.—Our hypothesis is that the effect of carbon chain length on oxidation in contrast with its small effect on pyrolysis is connected with the stability of the labile peroxide. A slight change in the structure of the hydrocarbon will affect the terms $k_3/(k_3+k_4)$ and $k_5/(k_5 + k_6)$. From the form of (1) it appears that small changes in these may have a greatly magnified effect on the rate.

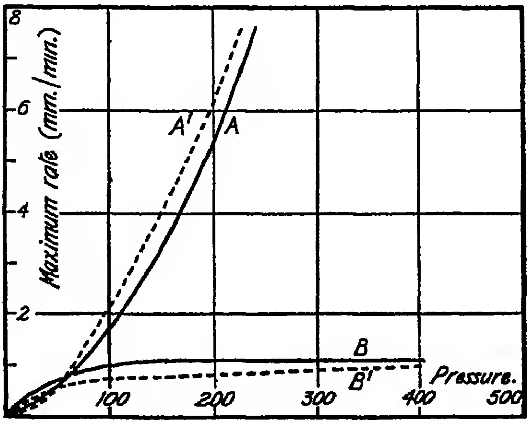


Fig. 6.—Comparison of experimental and theoretical curves for pentane oxidation.

A. Pentane varied (obs.): A′ (calc.).
B. Oxygen varied (obs.): B′ (calc.).
Temperature 227° c.

(2) Induction Period.—The reaction rate at time t is given by $p = p_{\text{max.}}(1 - e^{-At})$. When At is small this may be written approximately $p = p_{\text{max.}} At$. The induction period is a matter of somewhat arbitrary definition. If θ is the time required for the reaction rate to increase to a standard value $\bar{p}$, then

$$1/\theta = p_{\text{max.}} A/\bar{p}.$$

But $p_{\text{max.}}$ = constant . ϕ/A, so that $1/\theta$ should be proportional to ϕ. Now our experimental criterion of the end of the induction period is practically indistinguishable from that just defined, since the speed changes rapidly once perceptible reaction sets in. Since $1/\theta$ is not far from directly proportional to $[O_2]$ and to [RH], we shall take ϕ to be of the form $C_1[O_2][\text{RH}]$. For this reason (1*b*) is preferred to (1*a*) as the initiation reaction.

(3) Maximum Rate of Reaction.—Substituting the value just adopted for ϕ in (1) we obtain

$$p_{\text{max.}} = \frac{C_1[\text{RH}][\text{O}_2]}{1 - \dfrac{C_2[\text{RH}]}{[\text{O}_2] + C_3[\text{RH}]}} \quad . \quad . \quad . \quad . \quad (2)$$

Fig. 6 shows that this expression predicts results of the same general form as those found. The calculated values are taken from (2) with $C_1 = 1{\cdot}5 \times 10^{-5}$; $C_2 = 20{\cdot}0$; $C_3 = 20{\cdot}5$.

The form of (2), as it stands, predicts a branching-chain explosion at certain composition limits. This explosion, however, will be controlled by the quenching action of the formaldehyde produced in the reaction. The connection between the limit given by (2) and the "cool-flame" phenomenon is still under investigation and will not be discussed here.

(4) ANALYTICAL RESULTS.—The reaction scheme outlined is itself based partly upon the observation of the formation of peroxides and of formaldehyde in the early stages of the oxidation. Higher aldehydes can be formed from certain types of peroxide: e.g.

$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!CH—O—O—CH_2R_3 \text{ would give } R_1CHO + R_2 + CH_2O + R_3.$$

This is not unlikely, since free radicals probably attack hydrocarbon molecules more readily at secondary than at primary carbon atoms.[23] The equation written down shows how formaldehyde and higher aldehydes could, in appropriate circumstances, be formed in more or less equivalent amounts. The higher aldehydes, judging from their effect as additions, play no important part except that they are rapidly oxidised to acids which accumulate steadily.

(5) INHIBITORS AND ACCELERATORS.—The inhibition by HCHO can be ascribed to the reaction $R + HCHO = RH + HCO$. This would account for the gradual destruction of the formaldehyde during the induction period which it causes. The powerful accelerating influence of acetaldehyde on the oxidation of the "spectroscopic" hexane is to be attributed to its ability to destroy the other inhibitors which must be present in the impure hydrocarbon. With pure pentane and hexane the aldehyde is found to oxidise more or less independently as already explained. Alcohols do not affect the oxidation. Fresh measurements have confirmed the result[24] that higher alcohols are considerably less easily oxidised than the corresponding paraffins. The accelerating influence of a normal paraffin on the oxidation of its isomers is probably attributable to the greater ease of breakdown of the peroxidic substances formed.

We are indebted to Imperial Chemical Industries and to the Anglo-Iranian Oil Company for gifts of pure specimens of hydrocarbons.

This work is part of the programme of the Fuel Research Board, and is published with the approval of the Director of Fuel Research.

Summary.

The rate of oxidation of paraffins, in contrast with their pyrolysis, increases rapidly with the length of the uninterrupted carbon chain. An attempt is made to construct a simplified theory of the oxidation, based essentially upon Semenov's "slow-branching" mechanism, and assuming the latter to depend upon the splitting of unstable peroxides into alkoxy radicals, which are themselves labile and lose formaldehyde by simple electronic rearrangement. The salient facts with which the theory (and the new experimental work) deal are: the influence of the length of hydrocarbon chain, the induction period, the contrasted effects of oxygen and hydrocarbon pressure on reaction rate, the influence of inhibitors, and the early formation of HCHO in the reaction.

Résumé.

Le vitesse d'oxydation des hydrocarbures saturés croît rapidement avec la longueur de la chaîne de carbone. On suggère une théorie simplifiée de l'oxydation, basée sur un mécanisme à "ramification lente" lui-même dépendant de la coupure de peroxydes instables en radicaux oxyalcoyles, qui perdent de la formaldéhyde par simple réarrangement électronique. La théorie explique l'influence de la longueur de la chaîne de l'dydrocarbure, les effets contraires de la préssion de l'oxygène et d'hydrocarbure sur la vitesse de réaction, l'influence d'inhibiteurs et la formation de HCHO dès le début de la réaction.

[23] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 269.
[24] Layng and Youker, *Ind. Eng. Chem.*, 1928, **20**, 1048; Kane, Chamberlain and Townend, *J. Chem. Soc.*, 1937, 436.

Zusammenfassung.

Die Geschwindigkeit der Oxydation von Paraffinen wächst rasch mit der Länge der ununterbrochenen Kohlenstoffkette an. Es wird eine vereinfachte Oxydationstheorie vorgeschlagen, die auf einem Mechanismus mit langsamer Kettenverzweigung beruht, der seinerseits von der Spaltung instabiler Peroxyde in Alkoxyradikale, die dann durch einfache Elektronenumordnung Formaldehyd verlieren, abhängt. Die Theorie erklärt den Einfluss der Länge der Kohlenwasserstoffkette, den Kontrast der Abhängigkeit von Sauerstoff- und Kohlenwasserstoffdruck auf die Reaktionsgeschwindigkeit, den Einfluss von Verzögerern und die frühzeitige Bildung von Formaldehyd in der Reaktion.

PART IV.—OXIDATION OF LOWER PARAFFINS.

By M. F. R. Mulcahy.*

Received 23rd July, 1947.

In experiments described in Part III the rates of oxidation of a number of paraffin hydrocarbons were measured under comparable conditions. It was shown that from pentane to decane the oxidation rate increases rapidly with the length of the carbon chain. The work reported in this paper extends the general comparative survey to the lower members of the series, viz. *n*-butane, propane and ethane.

Experimental.

The apparatus and experimental method were similar to that referred to in the previous part, the maximum rate of pressure increase being taken as a measure of the rate of reaction. The (cylindrical, silica) reaction vessel was somewhat smaller: 6 cm. diam. × 10 cm. It was necessary to "acclimatise" the vessel to each hydrocarbon by carrying out a number of preliminary runs in it, before reasonably consistent values for the rate and particularly the induction period could be obtained.

The Relative Oxidation Rates of *n*-Pentane, *n*-Butane, Propane and Ethane.

As with the higher members of the series, it was not found possible to measure oxidation rates for more than two hydrocarbons at the same temperature, since the temperature interval for each hydrocarbon between infinitesimal reaction and the appearance of a cool flame or explosion is too small. The hydrocarbons have therefore been taken in pairs and the rates compared in each case at a convenient common temperature. This introduces a certain arbitrariness into the results since, as will be seen, the temperature coefficient of reaction rate is not the same for each hydrocarbon. Moreover the comparisons have been made for the most part at a single hydrocarbon/oxygen pressure ratio (30 mm. H.C./ 250 mm.O_2). Consequently the figures given should be taken as giving only an order of magnitude for the relative reaction rates.

In Fig. 1 the logarithm of the maximum rate, $\log_{10} \dot{p}_{max.}$, has been plotted against $1/T$ for mixtures of 250 mm. oxygen with 30 mm. ethane, propane and *n*-butane respectively. The point on the extreme right, which represents several measurements, refers to a similar mixture with *n*-pentane at a single temperature (263° C.). With propane below about 300° C. the induction periods became inconveniently long (> 24 hr.). Consequently for measurements at these temperatures the propane received an addition of 1 % acetaldehyde which considerably shortened the induction period. As far as can be seen from measurements at temperatures where it was possible to compare the rates with and without it, the 1 % acetaldehyde makes no appreciable difference to the rate (Fig. 1, cf. also Pease [1]). Because of the great difference between the reactivities of propane

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[1] Pease, *Chem. Rev.*, 1937, 21, 279.

and ethane it is necessary to compare extrapolated values of the rates. The comparison has been made mid-way between the highest and lowest temperatures available for each hydrocarbon respectively and, although the extrapolation of the propane curve is rather uncertain, the figure obtained is reliable at least as regards order of magnitude. Table I gives the relative reaction rates obtained from comparisons made at the temperatures indicated by the arrows in Fig. 1.

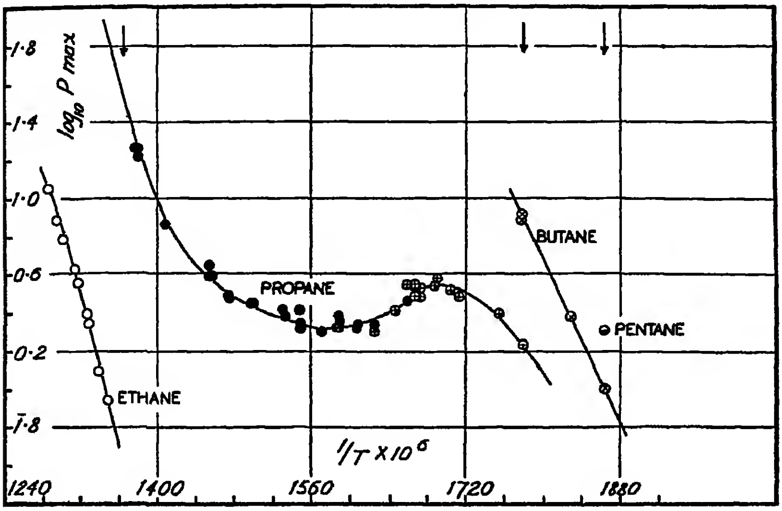

FIG. 1.—Propane curve: Crossed circles, with 1 % CH_3CHO; Black circles, without CH_3CHO.

It is clear that the reaction rate increases steeply with the chain length of the hydrocarbon. This is in accord with the general behaviour of the higher hydrocarbons described in the previous part.

The ($\log p_{max.}$) — $1/T$ curve for propane is interesting since it shows that with increasing temperature the reaction rate passes through a maximum at about 320° C. and then for the next 40° shows a negative temperature coefficient until at about 360° it begins to increase again. Similar behaviour over roughly the same temperature interval has been found by Pease [2] working with higher pressures of oxygen and propane. The phenomenon seems to be characteristic of paraffin hydrocarbons in general and is usually assumed to mark the temperature range in which the oxidation changes over from the "low-temperature" to the "high-temperature" mechanism.[2,3] It is generally accepted that ethane (and methane) in the absence of other substances, is only capable of reacting by the high-temperature mechanism, and in fact the kinetics of the oxidation of ethane show a number of fairly well-defined differences from those characteristic of the higher paraffins (cf. Prettre [4] and below).

TABLE I.

Temperature.		*Ratio of Reaction Rate.*	
263° C.	*n*-Pentane : *n*-Butane	2	1*
289° C.	*n*-Butane : Propane	5	1
461° C.	Propane : Ethane	90	1

* Comparison of 50 mm. hydrocarbon/200 mm. oxygen mixtures at 257·5° and at 261·5° also gave this ratio.

[2] Pease, *J. Amer. Chem. Soc.*, 1938, 60, 2244.

[3] Newitt and Thornes, *J. Chem. Soc.*, 1937, 1669.

[4] Prettre, *Acta Physicochim.*, 1938, 9, 581.

Some Experiments on the Influence of the Concentrations of the Reactants on the Maximum Rate and the Induction Period for Butane and Ethane.

In Fig. 2 and 3, which refer to butane and ethane respectively, the maximum rate ($\rho_{max.}$), the reciprocal of the induction period ($1/\theta$), and the final pressure reached on complete reaction (Δp_{∞}) are plotted against the initial partial pressure of each of the reactants.

BUTANE (Fig. 2). The *rate* rises rapidly with increasing initial pressure of butane, the curve being of the form $\rho_{max.} = Ap^n$, where $n = 1{\cdot}7$. However, it would appear that no simple significance can be attached to the numerical value of n (or A). Another series of experiments with the reaction vessel in a less active state but otherwise under identical conditions gave a curve of essentially similar shape but with different values of A and n ($n = 2{\cdot}1$). The influence of oxygen concentration is quite different. The rate rises to a shallow maximum at about 100 mm. oxygen pressure and then very gradually decreases, i.e. beyond an oxygen/butane ratio of roughly 1·2 oxygen has a slight retarding effect on the rate. Experiments with 50 mm. butane and varying pressures of O_2 at 259° gave a similar result.

It will be seen from Fig. 2 that *the reciprocal of the induction period* (here defined as the time, in min., for the reaction to reach a standard rate, 0·5 mm./min.) increases linearly with both the oxygen and the hydrocarbon concentrations. The difference in behaviour between the maximum rate and the induction period in these circumstances is remarkable. Both as regards the dependence of the induction period and the rate on the reactant concentrations, the general behaviour of butane is very similar to that of hexane and pentane (see Part III).

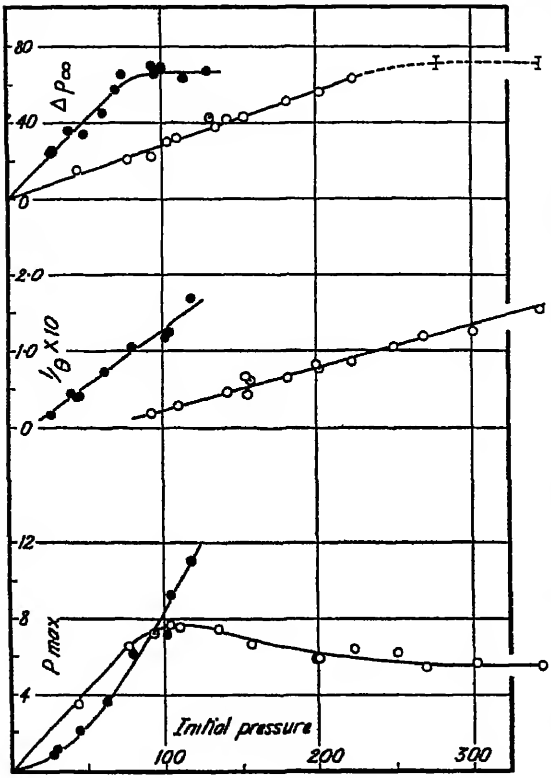

FIG. 2.

Open circles—variable O_2 (butane = 80 mm.).
Full circles—variable butane (O_2 = 250 mm.), 263° C.

Fig. 2 shows that the final pressure Δp_{∞} * increases linearly both with the oxygen and butane up to a maximum which, in each case, occurs close to the oxygen/butane ratio of 3 : 1. The same result was also obtained with 50 mm. butane and varying O_2 pressure at 259°.

ETHANE (Fig. 3).† Comparison of Fig. 2 and 3 will show that with ethane the general picture of the dependence of the rate and induction period on the

* Most of the points in the Δp_{∞} curves of Fig. 2 were obtained by extrapolation. This accounts for the scatter.

† These measurements are rather less accurate than the foregoing because of the high rates of reaction.

partial pressures of the reactants is different from the corresponding behaviour of butane and the higher hydrocarbons. The most notable point of difference is the effect of oxygen concentration. With ethane the rate increases with rather more than the first power of the oxygen pressure. This contrasts strongly with the slight retarding effect of oxygen in the butane experiments. The influence of hydrocarbon concentration also seems to be more marked, the apparent 'order' being between 2 and 3. Substantially similar results have been obtained for ethane at 450-460° by Taylor and Riblett.[5] A positive influence of the oxygen pressure on the rate of oxidation of propane at high temperatures has been observed by Newitt and Thornes[3] and by Pease.[2] Pease has pointed out that this is in contrast with the behaviour of the same hydrocarbon at lower temperatures where the rate is nearly independent of the oxygen concentration.

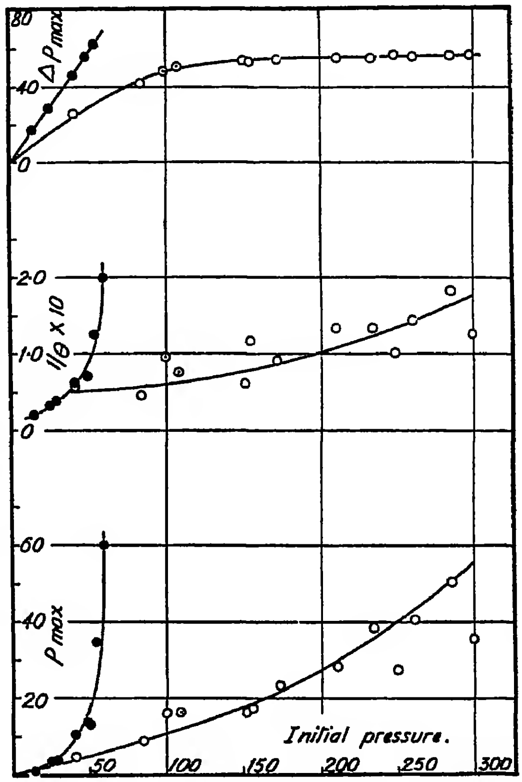

Fig. 3.

Open circles—variable O_2 (ethane = 50 mm.).
Full circles—variable C_2H_6 (oxygen = 250 mm.), 486° c.

Again in contradistinction to the higher hydrocarbons, a linear increase of $1/\theta$ with the reactant concentrations was not found for ethane at least as regards the effect of the hydrocarbon (Fig. 3). It appears that the rate of the initial stage of the reaction runs roughly parallel to the maximum rate. This further emphasises an important difference between the general kinetic schemes which obtain in the oxidation of ethane on the one hand and of the higher paraffins on the other.

Summary.

The steep gradation with carbon chain length of the oxidation rate of the higher hydrocarbons is continued in the series *n*-butane, propane, ethane. A comparative survey is made of the kinetics of the three reactions under comparable conditions.

Résumé.

La gradation rapide de la décomposition des hydrocarbures supérieurs avec la longueur de la chaîne de carbone est continue dans la série *n*-butane, propane, éthane. On donne un exposé comparatif de la cinétique de ces trois réactions dans des conditions comparables.

[5] Taylor and Riblett, *J. Physic. Chem.*, 1931, 35, 2667.

Zusammenfassung.

Die jähe Abstufung des Zerfalls der höheren Kohlenwasserstoffe mit der Länge der Kohlenwasserstoffkette wird in der Serie *n*-Butan, Propan, Äthan fortgesetzt. Es wird ein Überblick über die Kinetik der drei Reaktionen unter vergleichbaren Bedingungen gegeben.

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THE MEASUREMENT OF FAST REACTIONS OF ATOMIC HYDROGEN.

By J. C. Robb and H. W. Melville.

Received 26th June, 1947.

In homogeneous gas reactions it has become increasingly apparent that one of the important controlling steps is the interaction of atoms or radicals with molecules. Such interactions may result in exchange, dehydrogenation, or addition if the molecule is unsaturated. The present paper deals with the third type of process. The addition reaction while of great intrinsic interest is also the main step in the polymerisation of ethylenic compounds. The simplest type of radical-double bond interaction is the addition of atomic hydrogen to ethylene and the logical extension is the examination of this interaction with ethylene derivatives in order to determine quantitatively how the structure of ethylene compounds will affect the reactivity of the double bond.

Hitherto the velocity of such an elementary reaction has not been determined since it is so great. In all experiments which have so far been done the rate of addition has been wholly determined by the rate of production of atomic hydrogen, simply because all the hydrogen atoms generated have disappeared by the reaction with ethylene. It is this fact that automatically precluded the measurement of a velocity coefficient. In order to measure such a coefficient, it is necessary to arrange matters so that a competing reaction for hydrogen-atom removal operates simultaneously, the velocity coefficient for the competing reaction being known accurately. The problem here is to choose such a competing reaction for it is believed that the efficiency of the uptake of atomic hydrogen by ethylene is very high. The convenient para hydrogen method cannot, unfortunately, be used, for the collision of $H + H_2 \rightarrow H_2 + H$ is too low at 10^{-7} at 20° c. The reaction which has been chosen to solve this problem is the uptake of atomic hydrogen by molybdenum oxide, MoO_3.

Experimental.

It is well known that molybdenum oxide,[1] a light yellow powder, has the property that it can add on hydrogen atoms very easily and in so doing turns blue. This seemed to be a possible means of providing a competitive hydrogen atom-removing reaction. It had, however, to be shown that all hydrogen atoms striking the surface were removed, and further that the glass surfaces of a reaction vessel would act as a perfect reflector.

These facts were verified by measuring the quantum input to a parallel-walled reaction vessel, 2 cm. deep, by two methods. The first method was that described by Birse and Melville,[2] making use of the kinetics of the conversion of para hydrogen to ortho hydrogen. The other measurement was made by covering the bottom of the reaction vessel with MoO_3 and measuring the rate

[1] Johnson, *J. Franklin Inst.*, 1929, **207**, 629; 1930, **210**, 135.
[2] Birse and Melville, *Proc. Roy. Soc.*, *A*, 1940, **175**, 187.

of pressure drop. By assuming that each hydrogen atom generated is removed on the oxide layer and that each quantum produces 2 hydrogen atoms, the quantum input can be calculated. Table I shows the satisfactory agreement between the two methods of estimation.

TABLE I.

Method of Measurement.	*Quantum Input.*
Conversion of para hydrogen	$2 \cdot 87 \times 10^{16}$ quanta/sec.
Rate of removal ot hydrogen on MoO_3 . . .	2.81×10^{16} quanta/sec.

The agreement of the two estimates indicates that the assumptions are justified, i.e.,

1. all hydrogen atoms generated are removed on the oxide surface ;
2. no hydrogen atoms recombine on the glass walls of the reaction vessel at the expense of the oxide surface.

The maximum pressure of hydrogen used in these investigations was 10 mm.

Reaction Vessel.—In order to be able to alter at will the efficiency of the competitive removal of hydrogen atoms on a molybdenum oxide surface, it was decided to construct a reaction vessel so that the life-time of a hydrogen atom could be shortened or lengthened according to the type of reaction being studied.

The final design is shown in Fig. 1. The body of the reaction vessel A was formed from the neck of a bolt-head flask which had a conveniently wide flange on top. The side-tube is fitted with a ground glass cone C, to facilitate removal of the whole reaction vessel from the rest of the apparatus. F is a shallow glass dish supported on four springs screwed into a brass holder G. The spacing of the glass plate is maintained at a predetermined distance from the silica window E, by four small glass blocks. A ring of soft glass is fitted on top of the silica window to limit the generation of active centres to the volume directly above the glass dish, which, when the apparatus is in action, contains a layer of molybdenum oxide. The lower end of the brass spring holder is conically recessed and fits over a conical point above tube H. The purpose of this is to ensure that even if H is not truly perpendicular to the plate E, plate F will still automatically take up a position parallel to E at the predetermined spacing and will be firmly held by the springs. Column H consists of a brass tube internally screwed and fitted with three flutes for the purpose of locating the tube in the centre of the lower part J, and at the same time allowing adequate space for diffusion from J into the body of the vessel. A small indentation is made in the glass part J so that the fluted tube cannot rotate within the vessel. Another brass rod, screwed to fit inside H is fitted so that it can be turned by rotating the ground glass joint B. In this way, the plate F can be raised or lowered at will and set at any depth in the reaction vessel.

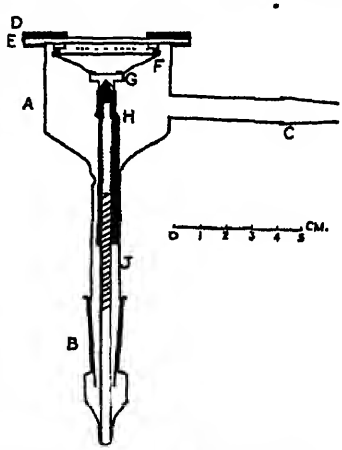

FIG. 1.—Variable path reaction vessel.

Analytical Methods.

Two methods of dealing with the analysis of the reaction mixture to determine the extent of removal of the double bonds have been devised. In the first, the actual number of double bonds used up are estimated and in the second, the number of hydrogen atoms which reach the molybdenum oxide surface is measured.

In the measurement of the number of double bonds used, a McLeod gauge was modified by removing the compression capillary limb and replacing it by a piece of thin glass tubing with a No. 10 ground glass socket. A silica tube, closed at one end, is sealed to a No. 10 silica cone and fitted to the socket. It is then possible to compress a sample of double bonds and hydrogen into the thimble, irradiate the mixture with light at 2537 A. and from the drop in pressure

calculate the percentage of double bonds in the mixture. By taking a sample from the reaction vessel before and after a run, the amount of hydrogen atoms used up in the actual hydrogenation can be estimated and applied to the calculations.

The other method is to estimate the actual number of hydrogen atoms which are added on to the molybdenum oxide. This is done by following the colour change of the oxide as the hydrogen atoms add on. The apparatus is shown in Fig. 2. It consists of a 25 w. lamp A, silvered except for a small aperture through which light is projected along tube B and directed by means of a small polystyrene prism-lens combination D, on to the oxide surface at E. The reflected light is measured by the photo-electric cell C and as the surface becomes more and more blue, the intensity of the reflected light becomes less. It is found that by suitable adjustment of scales a linear relationship can be obtained by plotting the current or voltage developed by the cell against the logarithm of the time of irradiation. The lamp intensity is maintained constant by eliminating voltage fluctuations by a voltage stabiliser.

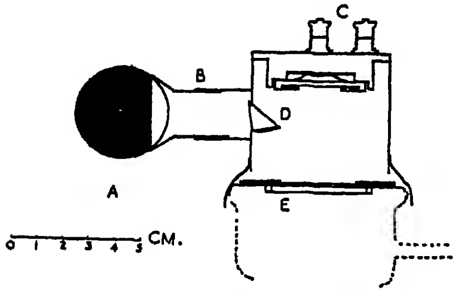

FIG. 2.—Apparatus for the determination of the colour of molybdenum oxide.

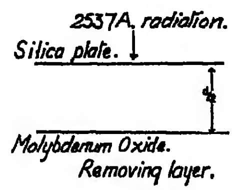

FIG. 3.—Theoretical diagram of reaction system.

Theoretical.

The method of approach which was considered to be the easiest and at the same time most absolute was to make use of the stationary-state differential diffusion equations. This method has been treated by Semenoff [3] for a limited number of conditions. His theoretical methods were devised to deal with chain reactions, but they are easily shown to be equally applicable to the diffusion of active centres, such as hydrogen atoms or radicals, through a gas mixture.

The experimental conditions are as follows. Consider a reaction vessel as in Fig. 3 with a top window of silica to permit the passage of 2537 A. radiation to produce excited mercury atoms to generate the necessary active centres by collision and transference of energy. It may be mentioned here that of all the methods available for the generation of hydrogen atoms the most convenient for absolute study seems to be the mercury-photosensitised. It avoids also the necessity for a flow system and tends to make the experimental manipulation easier. The bottom surface of the reaction vessel is a perfect trap for the active centres, removing each active centre as it collides with the surface. The amount of radiation absorbed per unit volume will vary exponentially throughout the vessel and hence the number of active centres generated at any particular point will vary.

Now in any layer, we have active centres being destroyed by collision with unsaturated molecules. The rate of removal will be given by

$$-\,d(H)/dt = k_t(H)(X)$$

where k_t is the velocity constant of the reaction and (X) the concentration of the removing agent. For convenience let $k_t(X) = g$. Then the number

[3] Semenoff, *Chemical Kinetics and Chain Reactions.*

of hydrogen atoms removed per cc. per sec. will be g(H) or in the more general case where n is the concentration of the active centres, gn is the number of active centres removed per cc. per sec.

In the stationary state, when the rate of removal of active centres is equal to the rate of generation, we can get from diffusion theory the following differential equation.

$$D(d^2n/dx^2) + I_0kce^{-kx} - gn = 0, \quad . \quad . \quad . \quad (1)$$

where c is the number of active centres produced per quantum and k the extinction coefficient for mercury vapour. Now let $b^2 = g/D$. The solution of this equation is

$$n = \frac{I_0kc}{D(k^2 - b^2)}\left[\frac{\cosh bx}{\cosh \frac{bd}{2}} e^{-\frac{kd}{2}} + \frac{k}{b} \cdot \frac{\sinh b\left(\frac{d}{2} - x\right)}{\cosh \frac{bd}{2}} - e^{-kx}\right] \quad . \quad (2)$$

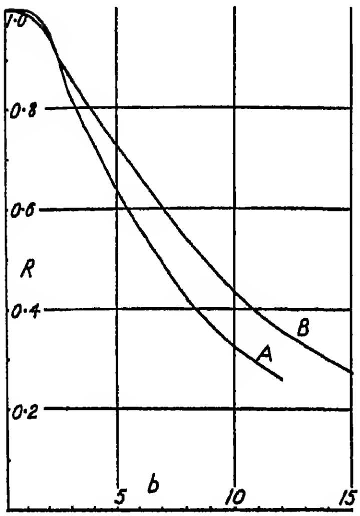

FIG. 4.—Relationship between R and b —see equation V.

Cell thickness—h: 5·0; A: 0·25 cm.; B: 0·20 cm.

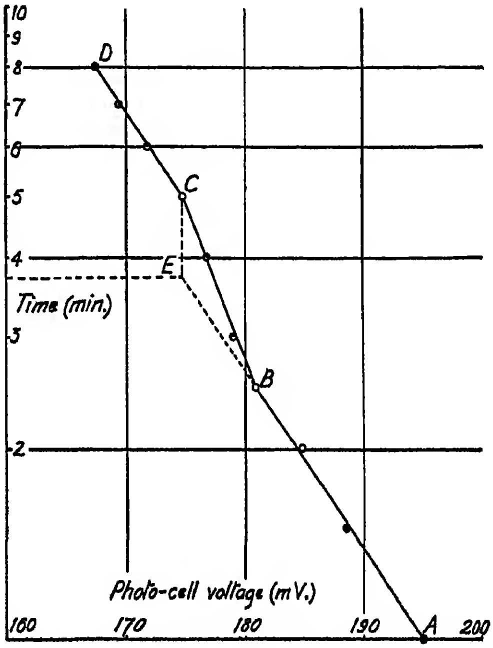

FIG. 5.—Change of blueness of molybdenum oxide.

Now the diffusion coefficient D is defined by

$$N = -D(dn/dx)_x \quad . \quad . \quad . \quad (3)$$

where N is the actual number of active centres which pass through the plane x in unit time and (dn/dx) is the concentration gradient at a point distant x from the incident plane of irradiation. Differentiating eqn. (2) and multiplying by D,

$$-N = \frac{I_0kc}{(k^2 - b^2)}\left[\frac{b \sinh bx}{\cosh \frac{bd}{2}} e^{-\frac{kd}{2}} - k \cdot \frac{\cosh b\left(\frac{d}{2} - x\right)}{\cosh \frac{bd}{2}} + k e^{-kx}\right] \quad (4)$$

If $x = d/2$, where $d/2$ is the depth of the reaction vessel, we get the number of atoms which actually reach the removing layer of molybdenum oxide.

If we further let the ratio of the number of atoms which reach the oxide to the number produced be R, then the following relationship is obtained :

$$-R = \frac{k}{\left(1 - e^{-\frac{kd}{2}}\right)(k^2 - b^2)} \left[\frac{b \sinh \frac{bd}{2}}{\cosh \frac{bd}{2}} \cdot e^{-\frac{kd}{2}} - \frac{k}{\cosh \frac{bd}{2}} + k\, e^{-\frac{kd}{2}} \right] \quad (5)$$

The best method of solving this equation for b is to graph the value of R for various values of b. By suitable choice of conditions a curve can be obtained as in Fig. 4 to cover the range of b required for a change of R from 0·25 to 0·75. The value of R can be measured, and from the curve, the corresponding value of b may be obtained. Hence, knowing the value of D, g is determined. From this value, knowing the concentration of X, the velocity constant is evaluated.

Since $k_t = z \times$ collision efficiency, where z is the collision number and is calculated from

$$z = \sigma^2 \left\{ 8\pi RT \left(\frac{M_H + M_X}{M_H \cdot M_X} \right) \right\}^{\frac{1}{2}}$$

where σ is the mean collision diameter of the two particles H and X, the collision efficiency of the reaction is obtained.

TABLE II.

Run.	$p(C_3H_6)$. (mm.).	$p(H_2)$ (mm.).	$p(H_2)$ Dissociated (mm.).	$p(C_3H_6)$ Used (mm.).	Coll. Eff.
1	0·8	5·4	0·38	0·5	$1 \cdot 1 \times 10^{-4}$
2	0·7	5·2	0·38	0·47	$1 \cdot 1 \times 10^{-4}$
3	0·75	5·6	0·38	0·34	$1 \cdot 4 \times 10^{-4}$

A typical run is shown in Fig. 5 where the change in the rate of blueing of molybdenum trioxide in presence of a hydrogen atom-removing agent is observed. BE represents the course of the change of blueness in absence of a gas-phase removing agent and BC the course in presence of the agent. From these the relative times to reach the same degree of blueness can be obtained and hence the ratio of the number of atoms reaching the layer to the total number produced.

It has been discovered that in the case of butyl radicals and methyl radicals, although they add on to molybdenum oxide, they do not affect the degree of blueness to any appreciable extent.

Results.

The above methods have been explored in a preliminary fashion with propylene. During initial experiments a model reaction vessel was made up from a filter funnel with a glass plate inserted 2 mm. from the rim and then the silica plate fastened on with Picien wax. The analytical method of measuring the number of double bonds hydrogenated was adopted. The quantum input could be obtained by carrying out a run with hydrogen and measuring the rate of pressure-drop in the reaction vessel. Table II shows the results obtained.

TABLE III.

Run.	Collision Efficiency.
4	$1 \cdot 0 \times 10^{-4}$
5	$0 \cdot 8 \times 10^{-4}$

By using the new reaction vessel and the colorimetric technique, concordant results have been obtained as shown in Table III. It is seen that the agreement is quite satisfactory, in view of the fact that two different techniques have been adopted and in two different reaction vessels. It is predicted that with suitable adjustment of conditions, collision efficiencies in the range of 10^{-2} to 10^{-7} can be measured.

We wish to thank the trustees of the Carnegie Trust for the award of a scholarship to one of us (J. C. R.).

Summary.

Hitherto, the velocity constant of the simple addition of a hydrogen atom to an unsaturated compound has not been accurately determined since the reaction occurs very rapidly. The main difficulty has been to get an efficient competitive reaction which is capable of accurate control and measurement. In this method the removal of hydrogen atoms on molybdenum oxide (MoO_3) is described and utilised to provide the competitive removal reaction.

A new type of reaction vessel is described by means of which the lifetime of a hydrogen atom can be altered as required by varying the path-distance of the hydrogen atom. This is done by raising or lowering a plate covered with molybdenum oxide.

A method is also described for measuring the percentage of double bonds present in a mixture of olefin, saturated hydrocarbon and hydrogen by hydrogenating the double bonds by mercury-photosensitised dissociation of molecular hydrogen.

The amount of atomic hydrogen removed on the molybdenum oxide surface is estimated by a colorimetric technique by measuring light reflected from the surface.

The application of these methods is discussed and illustrated by measurements made of the collision efficiency for the addition of a hydrogen atom to a propylene molecule.

Résumé.

On a mesuré la constante de vitesse pour l'addition d'atomes d'hydrogène à des composés non saturés par une réaction de compétition, MoO_3 enlevant les atomes d'hydrogène—on décrit comment mesurer le pourcentage de composé à double liaison, présent dans un mélange d'oléfines, d'hydrocarbures saturés et d hydrogène, par hydrogénation au moyen de la dissociation photosensibilisée au mercure d'hydrogéne moléculaire. La mèthode est appliquée, par exemple, aux mesures de la fréquence de chocs dans l'addition d'un atome d'hydrogène à la molécule de propylène.

Zusammenfassung.

Die Geschwindigkeitskonstante der Addition von Wasserstoff an ungesättigte Verbindungen wurde dadurch gemessen, dass eine kompetierende Seitenreaktion für die Wasserstoffatome, nämlich ihre Entfernung durch MoO_3, geschaffen wurde. Die Messung des Perzentgehaltes an Doppelbindungskörpern in einem Gemisch von Olefin, gesättigten Kohlenwasserstoffen und Wasserstoff, das durch Hydrierung mit Hilfe der durch Quecksilber sensibilisierten photochemischen Dissoziation von molekularem Wasserstoff erhalten wurde, wird beschrieben. Als Beispiel der Anwendung der Methode werden Messungen der Stosshäufigkeit für die Addition von Wasserstoffatomen an das Propylenmolekül beschrieben.

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GENERAL DISCUSSION.

Dr. H. Steiner (*Manchester*) said: With reference to Prof. Hinshelwood's questions regarding the low steric factors of reactions of hydrogen atoms and also of methyl radicals with hydrocarbons, may I put forward a suggestion, which, though probably not applicable to the reactions of methyl radicals, may be of importance in the case of the hydrogen atom reactions. Some years ago Prof. Rideal and I, when investigating exchange reactions of deuterium and hydrogen chloride [1] were led to study the transition complex H—Cl—H using the semi-empirical method of Eyring,[2] this complex being typical of exchange reactions of the type,

[1] Steiner and Rideal, *Proc. Roy. Soc. A*, 1939, 173, 503.
[2] For references, see Glasstone, Laidler and Eyring, *The Theory of Rate Processes* (McGraw-Hill, 1941).

$D + ClH \rightarrow DCl + H$. We found that the transition complex had considerable stability and should be formed readily because of a low activation energy associated with its formation. Yet experimentally it was found that this reaction does not occur. It is likely that this is due to a very low "transmission coefficient", the deuterium atom instead of reacting being reflected back. Applying to the potential-energy diagrams the rolling-ball picture of Petzer and Wigner,[2] one finds that because of the disparity of masses between the attacking deuterium atom and the central chlorine atom in the complex the energy of reaction cannot be dissipated but remains concentrated as vibrational energy of the newly-formed D—Cl link. As a consequence the D atom splits off again and no reaction occurs. In the reactions studied by Melville and Robb [3] particularly, a similar disparity of masses exists between the attacking hydrogen atom and the carbon atom of the olefine, with which it is to form a link. It may be that for this reason it is difficult to transmit the energy in the newly-formed link and as a result the probability of stabilising the corresponding molecular complex is small. This effect should manifest itself as a low steric factor for these particular reactions.

Dr. J. Weiss (*Newcastle*) said: Prof. Hinshelwood has referred in his remarks to the important question of the two possible ways in which free radicals can interact, i.e. dimerisation and disproportionation. It is, of course, not possible to make any definite predictions regarding the behaviour of radicals although it is perhaps possible to outline a few general considerations.

Dimerisation is generally favoured in solution where a third body is practically always present. In the case of radicals with a dipole moment, as for instance OH, dimerisation of the radicals to form H_2O_2 is disfavoured as in this case the negatively-charged ends of the dipoles would have to approach each other to a distance where the valence forces come into play. In general, dipole radicals will tend to assume the position of lowest potential energy, i.e. $\begin{matrix} +\text{———} \\ \text{———} \\ -\quad\ \ + \end{matrix}$ which, obviously, favours disproportionation. Therefore, in all these cases if disproportionation is possible it will be favoured rather than dimerisation, which is in agreement with experiments.[4]

Dr. M. Szwarc (*Manchester*) said: The recombination of atoms is known to be a three-body collision or a wall reaction. It is assumed, however, that the recombination of two radicals can occur as a two-body collision if there are enough degrees of freedom among which the energy released in the association process can be dissipated. The kinetics of the pyrolysis of benzyl iodide, investigated by C. Horrex and myself, seems to indicate that the recombination of benzyl radicals is not an efficient process, and it is quite probable that it requires a third body. Even more clear evidence has been obtained by myself in the study of the *p*-xylyl radicals. These radicals were shown to disproportionate in the gas phase under a pressure of a few mm. Hg, no dimerisation was observed. However, in the liquid phase, where these radicals were produced by the thermal decomposition of acetyl peroxide in *p*-xylene as a solvent, the bulk of resulting product was found to be the dimer,

$$CH_3—C_6H_4—CH_2—CH_2—C_6H_4—CH_3.$$

We can conclude, therefore, that the two-body recombination of *p*-xylyl radicals is a rare event, but in the liquid phase where each collision is probably a three-body collision, the dimerisation occurs quite easily.

It seems that we can generalise these observations and state that the recombination of even complex radicals proceeds usually by the three-body mechanism, and the two-body recombination has an extremely small probability factor.

[3] Melville and Robb, this Discussion, p. 131.
[4] Cf. also Weiss, *Trans. Faraday Soc.*, 1940, 34, 856.

It seems that the results obtained by Bawn and Tipper in their investigation of CH_2 radicals can be interpreted as an interesting case of a three-body collision leading to two different products of reaction. The recombination of CH_2 radicals in N_2 is a three-body reaction :

$$CH_2 + CH_2 + N_2 \rightarrow C_2H_4 + N_2.$$

The same reaction in H_2 can lead to a recombination of either pair of reactors :

$$CH_2 + CH_2 + H_2 \begin{cases} \nearrow C_2H_4 + H_2 \\ \searrow CH_3 + CH_4 \end{cases}$$

If this is the case, then the C_2H_4/CH_4 ratio is independent of H_2 pressure, and this was actually stated by the authors.

Dr. C. F. H. Tipper (*Bristol*) (*communicated*) : In connection with the paper by Steacie, Darwent and Trost, information on the steric factor of the reaction between methyl radicals and hydrogen can be obtained from a calculation using the results of Bawn and Tipper.[5]

It is thought probable that when sodium is passed into excess methyl iodide in hydrogen the methyl radicals formed disappear by the two reactions,

$$(1)\ CH_3 + H_2 = CH_4 + H \quad k_1$$
$$(2)\ CH_3 + CH_3 = C_2H_6 \quad k_2.$$

Then

$$\frac{d[CH_4]}{dt} = k_1[CH_3][H_2]$$

$$\frac{d[C_2H_6]}{dt} = k_2[CH_3]^2.$$

Using the usual expression for k, $k = PZe^{-E/RT}$ where P is the steric factor,

$$\frac{d[CH_4]}{dt} = P_1Z_1e^{-E_1/RT}[CH_3][H_2]$$

$$\frac{d[C_2H_6]}{dt} = P_2Z_2e^{-E_2/RT}[CH_3]^2$$

dividing

$$\frac{[CH_4]}{[C_2H_6]} = \frac{P_1}{P_2} \cdot \frac{Z_1}{Z_2} e^{-(E_1-E_2)/RT} \frac{[H_2]}{[CH_3]}.$$

From experiments at a hydrogen pressure of 5·8 mm. and a temperature of 363° c. the ratio $CH_4/C_2H_6 = 3{\cdot}7$. $E_1 - E_2$ has been found to be about 9000 cal., and Z_1 can be taken as equal to Z_2.

The value of the stationary concentration of methyl radicals is somewhat uncertain, but a maximum value is about 10^{-2} mm. (sodium atom pressure). Inserting these values, P_1/P_2 is found to be about 2. If a lower value of CH_3 of 10^{-3} is taken, P_1/P_2 is 0·2. The values of P_1 and P_2 therefore appear to be of the same order of magnitude. P_2, the steric factor in the recombination of methyl radicals, is generally considered to be small[6] ($\sim 10^{-4}$) and thus the steric factor for the reaction of the radicals and hydrogen would seem to be small also.

Dr. H. Steiner (*Manchester*) said : It has been shown in this Discussion, particularly by Steacie,[7] that considerable differences exist in the reactivities of hydrogen atoms and of methyl radicals with the lower molecular weight hydrocarbons of the paraffin series. The opinion was expressed[8] that this is due mainly to differences in the reactivities of hydrogen atoms bound to carbon by primary, secondary and tertiary bonds respectively. This in turn can be correlated with the corresponding differences in the bond energies of these linkages as was revealed particularly by the later

[5] Bawn and Tipper, *Trans. Faraday Soc.*, this Discussion, p. 103.
[6] Bawn, *Trans. Faraday Soc.*, 1935, 31, 1536.
[7] Steacie, Darwent and Trost, this Discussion.
[8] Smith and Taylor, *J. Chem. Physics*, 1939, 7, 390.

work of Polanyi and collaborators.[9] I wish to report some calculations which Dr. Watson and myself have carried out based on experiments on chlorination of paraffins by Hass and collaborators.[10] The results further illustrate the variations in reactivities of primary, secondary and tertiary carbon-hydrogen bonds. The thermal chlorination of gaseous paraffins at temperatures of 200°-400° C. proceeds by a chain mechanism and it can be shown that the rate-determining step is the reaction of a chlorine atom with the hydrocarbon according to

$$Cl + RH \longrightarrow HCl + R \quad . \quad . \quad . \quad . \quad (1)$$

This is followed by the rapid reaction

$$R + Cl_2 \longrightarrow RCl + Cl \quad . \quad . \quad . \quad . \quad (2)$$

leading to the final substitution product.

In the case where reaction with hydrogen atoms on different positions of the same hydrocarbon molecule can take place one obtains different products, the ratio of which directly gives the ratio of the relative rates of reaction (1). Thus in the case of propane we obtain the monochlorination products 1- and 2-chloropropane respectively and the ratio of the yields of the two products directly gives the ratio of the rate of the reaction of a Cl atom with a primary or secondary hydrogen of propane. Whilst by this method it is impossible to obtain absolute reaction rates, the relative rates can be obtained with considerable accuracy. In some cases relative yields have been measured over a range of temperatures and it is then possible to obtain the differences of activation energies and temperature-independent factors separately. In the case of propane we find for the relative reactions of a chlorine atom with a primary and a secondary hydrogen respectively a difference of 1·3 kcal. in the activation energies, while the temperature-independent factors are very nearly equal. In the case of *iso*butane we find a difference of 1·7 kcal. in the activation energies for reaction with the primary and tertiary hydrogen atom respectively; again the temperature-independent factors are equal within the accuracy of the experiments. Assuming that for other hydrocarbons the ratios of the temperature-independent factors are in the same way approximately unity, we can also calculate the activation energy differences in cases where experiments were carried out at one temperature only. In this way, we obtain the following data:

n-butane $\Delta E_1{}^2 = 1{\cdot}3$ kcal./mole.
n-pentane $\Delta E_1{}^2 = 1{\cdot}1$,,
*iso*pentane $\Delta E_1{}^2 = 1{\cdot}1$,,
*iso*pentane $\Delta E_1{}^3 = 1{\cdot}7$,,

where $\Delta E_1{}^2$ and $\Delta E_1{}^3$ stand for the differences in activation energies of reaction with a primary and secondary, and with a primary and tertiary hydrogen respectively.

Generally it is seen that there is a difference of 1·1-1·3 kcal. for reaction with a primary and secondary hydrogen respectively, and a difference of 1·7 kcal. for reaction with a primary and tertiary hydrogen. These differences are large if compared with the absolute activation energies of these reactions, which though not well known are of the order of 8-10 kcal., but they are smaller than the differences in bond strength of these bonds as given by Baughan, Evans and Polanyi.[9, 11] These authors find a difference of 6 kcal. in the bond strength of the primary and secondary C—H bond in propane, and if it be assumed that the bond strength of the primary bonds in butane and *iso*butane are approximately equal, one obtains a difference of 8 kcal. in the bond strength of primary and tertiary bonds in *iso*butane.

[9] Baughan, Evans and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377.
[10] Hass, McBee and Weber, *Ind. Eng. Chem.*, 1936, **28**, 333.
[11] Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 19.

For reactions of Na atoms with alkyl halides of the type:

$$Na + ClR \longrightarrow Na^+Cl^- + R$$

Butler and Polanyi [10] found for a whole series of hydrocarbon radicals R an approximately linear relation between bond strength and activation energy of the type

$$\Delta E = \alpha \Delta H$$

where ΔE = difference of activation energy;
ΔH = difference of bond strength;

and α = constant. α was shown theoretically to have a value of about 0·3 and experimentally a value of 0·27 was found. It is of interest to apply this relation to the present results where data are available. One finds that in the case of propane $\alpha = 0{\cdot}22$ and in the case of *iso*butane $\alpha = 0{\cdot}21$. Thus the same relation seems to hold for these reactions though with a slightly lower proportionality constant. It must be noted that this is by no means to be expected since Polanyi's relation was derived under the assumption that little resonance occurs in the transition state, an assumption which is justified in the particular case of the sodium-flame reaction to which this relation was applied. In contrast to this, resonance should be expected to play an important part in lowering the energy level of the transition complexes of the present reaction, yet the proportionality between bond strength and activation energy still seems to hold with only a slightly lower proportionality constant. This result indicates that differences in the resonance energies of the transition complexes of a chlorine atom reacting with a primary, secondary or tertiary hydrogen respectively of a hydrogen carbon molecule either are non-existent or small enough to be neglected.

Dr. E. W. R. Steacie (*Ottawa*) said: The results given in Norrish and Porter's paper give quite a different view of the reactivity of methylene, and are thus quite important. The surprising thing is the number of ways in which they differ from previous work; a different life-time, lack of specificity of certain mirrors, inefficiency of lead mirrors with acetone, and a virtually bimolecular disappearance of radicals.

The light source was very powerful, and formally one could explain the difference if CH_2 was not removed by a wall reaction, but by a second-order gas reaction, the rate thus increasing with increasing methylene concentration. This would also explain the second-order nature of the loss of activity. However, it seems unlikely that the concentration here was higher than that in experiments in which methylene was produced by the *thermal* decomposition of ketene.

Dr. C. H. Bamford (*Maidenhead*) said: It is difficult to draw any conclusions about radical reactivities from measurements of half-lives unless the precise nature of the radical-destroying reactions are known. Norrish and Porter remark that "the reactions of methyl and methylene radicals with themselves occur with similar readiness under the same conditions." As a conclusion about the reactivities of the radicals this does not seem to be justifiable unless it can be shown that in Norrish and Porter's experiments both radicals disappear in homogeneous reactions. If wall processes are important, the observed rate of reaction will depend not only on the reactivity of the radicals, but also on their accommodation coefficients, and the accommodation coefficients of the carrier gases.

Hitherto it has been agreed that in experiments of this kind at room temperatures the radicals react mainly on the walls. Thus Paneth, Hofeditz and Wunsch [12] showed that heating the tube increases the life of free methyl, and attributed this to a reduction in the accommodation coefficient at high temperatures. Pearson, Purcell and Singh [13] concluded that methylene in diazomethane reacts with the latter on the walls.

[12] Paneth, Hofeditz and Wunsch, *J. Chem. Soc.*, 1935, 372.
[13] Pearson, Purcell and Singh, *ibid.*, 1938, 409.

Norrish and Porter's results at the higher light intensities given on page 98 do not allow of a definite choice between first- and second-order kinetics. The results for CH_3 taken as a whole give a better first-order plot. (The second-order plot is fairly satisfactory except for the 90 and 95 cm. points, which are a long way out.) Their experiments at lower intensities (Fig. 1 of their paper) give a good second-order plot. The results of Paneth (for CH_3) referred to above show an interesting similarity: for short distances (high concentrations) the order is nearly one, while for long distances it is almost two. These variations would seem to indicate that at high concentrations the radicals react by a first-order process, and at lower concentrations by a second-order process, and thus imply a wall reaction. The experimental indications are therefore that the termination reaction is complex in nature, and it is doubtful if the present technique is capable of providing clear-cut evidence as to the comparative reactivities of the radicals.

Mr. G. Porter (*Cambridge*) said: The differences in life-time and reaction-order mentioned by Dr. Steacie are not so surprising if we assume the following.

(*a*) The recombination of radicals in flow experiments occurs almost exclusively by the collision of a radical from the gas phase with one adsorbed on the wall.

(*b*) The concentration of radicals adsorbed on the walls is proportional to the pressure of radicals in the gas phase at low concentrations, the total gas pressure being kept constant, but reaches a saturation limit at higher concentrations.

Thus, at high partial pressures the reaction will follow a first-order law, but at low pressures the concentration adsorbed on the walls will be proportional to the partial pressure of radicals in the gas phase and the reaction will chang over to a second-order mechanism. The figure of about 5×10^{-3} sec. quoted by several workers for the half life-time of various radicals probably corresponds to the saturation part of the curve and is accompanied by a unimolecular law. From a comparison of concentration measurements, mirror-removal times and kinetics, it appears that the concentration of radicals in our experiments was not very high, despite the powerful lamp; this is quite probable as a relatively small area of the tube was illuminated and the lamp was an inefficient radiator in the region below 3000 A.*

These assumptions allow a fairly good description of the experimental data. As Bamford has pertinently pointed out, the kinetics of CH_2-removal change from 1st to 2nd order as the concentration in our experiments decreases. The removal of CH_3 also becomes bimolecular at lower concentrations. Similarly the failure of the unimolecular rate law found by Paneth [14] was accompanied by relatively low radical concentrations, though Paneth inclined to the idea that the reaction was always bimolecular and that the failure to notice departure from linearity was due to "shorter range of measurement and the strong scattering of individual points in the former work". Unfortunately no comparison with high concentration of methylene, obtained by *thermal* decomposition of ketene is possible as this reaction does not appear to produce methylene.[15]

The difference in specificity of metal mirrors is almost certainly due to mirror poisoning and different surface conditions, although we found that bismuth gave particularly reproducible results, and was as reliable as tellurium.

* In high-pressure mercury lamps of this type, the energy distribution is shifted towards the visible region. In addition, reversal of the 2536 A. line is complete and the absorption spreads over a considerable portion of the ultra-violet region.

[14] Paneth, Holfeditz and Wunsch, *J. Chem. Soc.*, 1935, 372.

[15] Pearson, Purcell and Saigh, *ibid.*, 1938, 409.

The comparison of radical reactivities on the basis of mirror experiments made by Pearson, ourselves and others does, as Dr. Bamford points out, depend on the assumption that the accommodation coefficients of the radicals compared is the same. It is, however, extremely improbable that under the varied conditions of our experiments the accommodation-coefficient differences should always compensate for the different reactivities of the radicals, nor is there any reason to suppose a vast difference in accommodation coefficients between CH_2 and CH_3, so that, as a test between free-radical or relatively stable molecular behaviour, we believe that the method is valuable. Any more quantitative interpretation of the results of mirror experiments, especially comparisons under different conditions of concentration and surface, must be accepted with reserve.

Dr. C. A. McDowell (*Liverpool*) (*communicated*) : Norrish and Porter in discussing the structure of methylene state that " in the singlet state we are dealing with bonds arising from a pure p carbon atomic orbital, whereas the bonds in the triplet structure can be sp diagonal hybrids " ; and as this seems to be a common belief it is perhaps necessary to point out that Mulliken [16] and Lennard-Jones [17] have shown by the methods of group theory that it is possible for the bonds in the singlet state of methylene also to be sp hybrids. The group theoretical treatment of this problem is very simple and goes along the following lines. The carbon atom, in its ground state, has one $2s$, and three $2p$ atomic orbitals available for bond formation, and the hydrogen atom has, of course, only a $1s$ orbital. When methylene is formed the orbitals available for bond formation are determined by the symmetry of this compound. There are only two possible structures for methylene (*a*) angular symmetric belonging to point group C_{2v} ; (*b*) linear symmetric belonging to point group $D_{\infty h}$. The angular symmetric form (C_{2v}) gives rise to the singlet state. The character table for group C_{2v} is shown above (Table I). Suppose we choose our co-ordinates as shown in Fig. 1(*a*) and then inquire how the $2s$, $2p_x$, $2p_y$, $2p_z$, atomic orbitals of the carbon atom behave under the operations of this group, i.e. we determine to which irreducible representation the various orbitals belong. This is important for it can be

TABLE I.—CHARACTER TABLE FOR SYMMETRY GROUP C_{2v}.

	E.	C_2.	σ_v.	σ_v'.
A_1 . .	1	1	1	1
A_2 . .	1	1	−1	−1
B_1 . .	1	−1	1	−1
B_2 . .	1	−1	−1	1

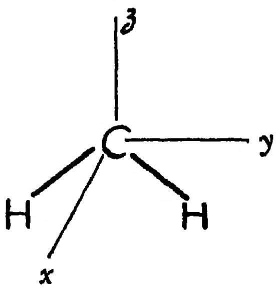

FIG. 1(*a*).—Methylene with symmetry C_{2v}.

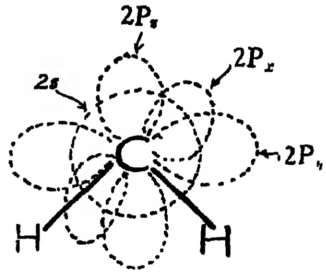

FIG. 1(*b*).—Showing the $2s$, $2p_x$, $2p_y$, $2p_z$, atomic orbitals of the C atom.

[16] Mulliken, *Physic. Rev.*, 1932, 41, 751.
[17] Lennard-Jones, *Trans. Faraday Soc.*, 1934, 30, 70.

shown that *when a bond is formed hybridisation can only occur between orbitals belonging to the same irreducible representation of the symmetry group of the resulting molecule.*

The $2s$ orbital of the carbon atom is spherically symmetrical and so obviously belongs to representation A_1. We shall represent the symmetry of the molecular orbital by small letters, hence we say that this orbital has symmetry a_1. Of the three $2p$ atomic orbitals of the carbon atom it is easily seen that they have the following symmetries, $2p_x \sim b_1$, $2p_y \sim b_2$, $2p_z \sim a_1$. Since the $2s$ and $2p_z$ orbitals belong to the same representation, a_1, hybridisation is possible when methylene with symmetry C_{2v} is formed, i.e. in the ${}^1A_1$ or singlet state.

The operations of rotation and reflection of this group turn one hydrogen atom into the other; and it is, therefore, necessary to take linear combinations of these two hydrogen orbitals. It can be shown by forming the direct products $\sum_i \chi_i(R)R\phi$ that the proper combinations are $H_A = H_B$. The former belongs to class a_1 while the latter belongs to class b_2. The a_1 orbitals are of two types which we shall call $(a_1)_1$ and $(a_1)_2$. Hence the following molecular orbitals are possible when methylene in the A_1 state is formed :—

$$(a_1)_1 = a(2s) + b(H_A + H_B) = c(2p_z)$$
$$(b_2) = d(2p_y) + e(H_A - H_B)$$
$$(a_1)_2 = f(2p_z) + g(H_A + H_B) + h(2s).$$

According to Mulliken and Lennard-Jones the C—H binding is governed by all three orbitals.

Dr. A. D. Walsh (*Cambridge*) (*communicated*) : It is clearly of the utmost importance to be sure of the origin of the sodium excitation energy in the experiments of Bawn and his collaborators : for the interpretation given by Bawn has a direct bearing on the structure of the methylene radical. Can we completely rule out the possibility that this excitation energy comes from the recombination of CH_2 radicals to give C_2H_4 ?

$$CH_2 + CH_2 + Na = C_2H_4 + Na^*. \quad . \quad . \quad . \quad (1)$$

The energy available is of course ample. Moreover, we need not suppose a triple collision (which has the objections already pointed out by Bawn and Dunning [18]) in the simplest sense. If two CH_2 radicals combine, the resulting C_2H_4 (even though excessively energy-rich) may have an appreciable life simply through some of its energy of formation passing into vibrational degrees of freedom and an appreciable time may elapse before the molecule again assumes the phase in which all the energy is available for decomposition. Minkoff [19] has described a similar process in the formation of energy-rich HO_2, so that the reaction

$$H + O_2 + M = HO_2 + M^* \quad . \quad . \quad . \quad (2)$$

commonly accepted as occurring in the H_2—O_2 reaction, need not involve a triple collision in the ordinary sense. Certainly, if energy-rich C_2H_4 is formed, it seems plausible that it should be capable of transferring energy to a sodium atom on collision for it has been shown [20] that the reverse process occurs readily. Evidently the relevant potential-energy surfaces are such that crossing is quite possible. On the other hand, the comparatively small radius of cross-section found for the quenching by C_2H_6 of sodium resonance radiation, means that transfer of energy from an energy-rich C_2H_6 molecule (in contrast to C_2H_4) to a sodium atom is hardly likely to occur. Thus the objection to (1) that

$$CH_3 + CH_3 + Na = C_2H_6 + Na^* \quad . \quad . \quad . \quad (3)$$

[18] Bawn and Dunning, *Trans. Faraday Soc.*, 1939, **35**, 185.
[19] Minkoff, this Discussion.
[20] Norrish and Smith, *Proc. Roy. Soc. A*, 1940, **176**, 295.

does not occur [18] hardly has much force. Energy transfers are highly specific and the clue to their likelihood with sodium may well be found in the converse *experiments on quenching of sodium radiation.*

Dr. C. E. H. Bawn (*Bristol*) said: Dr. Walsh has suggested that the triple-body collision process, $CH_2 + CH_2 + Na \rightarrow C_2H_4 + Na^*$, which was ruled out owing to its infrequency, might be replaced by the two-stage process

$$CH_2 + CH_2 \rightarrow CH_2{=}CH_2^* \quad . \quad . \quad . \quad . \quad (1)$$

$$CH_2{=}CH_2^* + Na \rightarrow Na^* + CH_2{=}CH_2 \quad . \quad . \quad (2)$$

in which energy-rich ethylene molecule may transfer its energy to a sodium atom. Assuming that (1) is possible, experiment and theory show that reactions of this type do not occur at every collision but have an appreciable steric factor. Under our experimental conditions, in which the total pressure was 0·001 to 0·01 mm., the mean-free-path of the CH_2 formed is of the order of the diameter of the reaction vessel and collisions leading to association would be extremely infrequent. The association reaction would most probably be a wall reaction, since other evidence indicates a high accommodation coefficient for CH_2, and under these conditions the excitation energy would be lost. The same argument applies to the second stage of the reaction and, even if we assume $CH_2{=}CH_2^*$ of long life, the energy exchange would be a very improbable process, owing to the very high frequency of wall collisions (pressure Na $= 10^{-3}$ mm.).

I agree that further information as to the nature of the energy-rich particle leading to *D*-line emission, viz. whether Na^* or $NaBr^*$, could be obtained from quenching measurements, and this was the method originally used with Na-halogen flames to prove that the energy-transfer agent was $NaHal^*$.

The absence of luminescence in reactions giving a monoradical (R) is of greater significance than is assumed by Dr. Walsh. In no case has luminescence been observed with associations of the type $R + R + Na \rightarrow R - R + Na^*$, and a very large number ($>$ 50) of radical types have been studied, including those containing double bonds.

Dr. E. W. R. Steacie (*Ottawa*) said: In connection with Part II of the paper of Hinshelwood *et al.* the results are in agreement with earlier investigations which indicated that the frequency factors remain approximately constant down the series, while the activation energy falls off to about C_4 and then remains virtually constant. If the relatively small inhibition by NO is taken at its face value, then the results for the uninhibited reaction are not much affected by chain processes. However, the falling-off in rate at low pressures for, say, *n*-butane is much too large for so complex a molecule, and would certainly indicate the "freezing" of most of the degrees of freedom. It seems to me, however, that there is considerable doubt if maximum inhibition really corresponds to the complete suppression of chains. In the case of *n*-butane there are three possible modes of decomposition: to $C_4H_8 + H_2$, $C_3H_6 + CH_4$, and $C_2H_4 + C_2H_6$. The products indicate that all three occur. However, it is known [21] that the products of the NO-inhibited reaction are identical with those of the uninhibited reaction. If the inhibited reaction is chain-free then the chain process and the non-chain processes must fortuitously lead to the same very complex mixture of products. It seems to me, therefore, most unlikely that the maximally inhibited reactions are simple unimolecular changes.

Dr. W. A. Waters (*Oxford*) said: The work of Cullis and Hinshelwood has indicated that the active peroxides involved in the vapour-phase oxidation of hydrocarbons undergo two types of breakdown. They may either give inactive products, or, alternatively, may split to two active products which cause chain-branching. In this connection the outcome

[21] Steacie and Folkins, *Can. J. Res.*, *B*, 1940, 18, 1.

of the study of the liquid-phase oxidation of tetralin by Dr. A. Robertson and myself is cogent. This first gives tetralin hydroperoxide, and we have shown that although the decomposition of this hydroperoxide in solution is substantially of first order, corresponding to the simple fission, R″CH—O—OH → R″CH—O• + •OH, only about 50 % of the radicals R″CH—O• and •OH appear to get "free" enough to react with adjacent solvent molecules by reactions of the general type,

$$RO^\bullet + H—X \rightarrow R—O—H + {}^\bullet X.$$

The remainder of the decomposition can be accounted for by the chain-breaking process R″CH—O• + •OH → R″C=O + H_2O between radicals which have not had time to separate.

Prof. Hinshelwood has stressed the point that gas-phase oxidations occur much more easily with normal paraffins than with branched-chain paraffins. Liquid-phase autoxidation gives exactly the opposite order of stability. However, these studies deal with peroxide formation rather than peroxide breakdown, and the facilitation of the complete vapour-phase oxidation may be due to the fact that secondary hydroperoxides, from normal paraffins, are much less stable than tertiary hydroperoxides, which would be formed from branched-chain paraffins.

Prof. Sir A. C. Egerton (*London*) said: Prof. Hinshelwood's contribution on "The kinetics of hydrocarbon reactions" is of much interest to me: particularly because of the work done in my department at the Imperial College by Dr. Harris and Dr. Young on the slow oxidation of butane and of propane. The main feature of that work was the analysis of the products of combustion at various stages of the oxidation by both chemical and absorption spectra methods. In all such work, I do not think we shall be on sure ground until the experimental facts are more definite, and our efforts on resuming such work are directed towards improving methods for the analysis of peroxides and aldehydes where they are present together in the products, as indeed they usually are. We find that aldehydes interfere with the determination of peroxides; for instance, for a quantity of aldehyde equal to that of ethyl hydrogen peroxide, only 59 % of the real amount of peroxide is obtained using the KI method (even with catalyst present). The dialkyl peroxides are particularly difficult to determine and the result of analysis is very sensitive to the quantity of iron catalyst needed to liberate iodine from the KI.

With the general scheme of oxidation and the importance of the alkyl peroxide radical (R—O—O•) and the radical $\begin{matrix} RC—O—O^\bullet \\ \diagdown O \end{matrix}$ from aldehydic oxidation, our work is in agreement, except that it seems to indicate a greater influence of the aldehydes (other than formaldehyde). The statement that methane gives rise to no peroxides is also not in agreement with certain experiments we have made, for, under certain circumstances, peroxides are formed during the oxidation of methane.

Anyone who has worked on the combustion of gases cannot otherwise than be impressed by the underlying similarity in their combustion behaviour, and it seems to me the underlying mechanism must be similar. The mechanism for hydrogen, for instance, has a close relation in forming the radical HO_2 with that of the hydrocarbons in forming such radicals as RO_2.

A molecule of a higher hydrocarbon when oxidised has to be stripped or "unravelled" so to speak. After the first few steps which give the peroxide radicals, that unravelling may be very rapid owing to the drastic decomposition of the peroxides (which may not exist as such for any appreciable time) into simple constituents, C_2H_5OH, CH_3CHO, CH_4, CO, CH_2O, H_2O, etc.

We are extending the studies of peroxide decomposition which Dr. Harris began: Dr. Emte has succeeded in making *n*-butyl peroxide and we are hoping to study its decomposition.

Mr. C. F. Cullis (*Oxford*) (*communicated*): Prof. Egerton has pointed out that the results reported in our paper [22] in regard to the influence of higher aldehydes on paraffin oxidation are in direct contrast to those obtained by him and his co-workers. Thus, for example, Pidgeon and Egerton [23] found that addition of valeric aldehyde decreased the induction period of pentane, whereas in our work neither acetaldehyde nor propionic aldehyde exerted any appreciable accelerating effect on the oxidation of this hydrocarbon. It is suggested that these differences may be explained in the following way.

At the comparatively low temperatures employed, aldehyde pyrolysis is normally negligible, but it is very markedly catalysed by the presence of oxygen. The accelerating influence of aldehydes may therefore be attributable to their decomposition reinforcing the normal supply of free radicals. If this is the case, the observed effect would presumably depend largely on the nature of the added aldehyde, this influence being determined by the length of the unbranched carbon chain in the free radical produced. Thus valeric aldehyde might be expected to yield peroxides of high reactivity under conditions where pentane oxidises rapidly, whereas the lower aldehydes would form peroxides which are comparatively stable at the temperatures concerned.

Dr. G. J. Minkoff (*London*) (*partly communicated*): In the initiation step of hydrocarbon combustion suggested by Prof. Hinshelwood

$$(RH + O_2 \rightarrow R^\bullet + HO_2,\ R^\bullet + O_2 \rightarrow ROO^\bullet,\ ROO^\bullet + RH \rightarrow ROOH + R^\bullet),$$

HO_2 and $R^\bullet$ are formed by the action of O_2 on the hydrocarbon molecule. The fate of the HO_2 will probably be to emerge, partly at least, as H_2O_2; the radical $R\cdot$ will now compete with the molecule RH for the remaining oxygen, the greater part of the oxygen now combining with the radical $R\cdot$ to give a peroxide radical and eventually an alkyl peroxide. During the initial stages of the oxidation, we should expect to find that the % H_2O_2 in the total peroxides found decreases as the reaction proceeds, or, for equal times of reaction, as the oxygen content of the mixture is increased. If the initiation is mainly due to hydroxyl radicals, water will be formed, and the peroxides found will contain little or no H_2O_2. These factors have been investigated by Kooijman,[24] who studied the peroxides formed when different propane-oxygen mixtures were heated to different temperatures for a time of 4 sec. The table above has been computed from his data.

Temp °c.	$\frac{H_2O_2}{\text{Total peroxides}} \times 100$.			
	6% O_2.	10% O_2.	20% O_2	30% O_2.
380	2	0	3	26
390	15	0	20	37
400	30	4 (?)	30	41
410	43	18	37	33
450	71	61	48	0
480	59	62	46	0

It can be seen from these results that at temperatures above 410° c., the criterion of initial attack by O_2 is fulfilled; below this temperature, a large proportion of oxygen must be present before H_2O_2 is found in the reaction product; it follows that at temperatures below *ca.* 400° c., another mode of initiation, presumably by OH, is of major importance in the oxidation of propane. These hydroxyl radicals may be formed from the decomposition of a few molecules of alkyl peroxides produced through initial attack by O_2, this process being so inefficient under these conditions as to become swamped by the "hydroxyl process". No

[22] Cullis and Hinshelwood, this Discussion, p. 116.
[23] Pidgeon and Egerton, *J. Chem. Soc.*, 1932, 661.
[24] Kooijman, *Dissertation* (Delft, 1942).

evidence is available for the combustion of higher hydrocarbons; it may be inferred, however, that molecules containing a greater number of more vulnerable secondary C—H bonds will be rather more easily attacked by oxygen molecules, so that initiation by O_2 will become more important at lower temperatures as the hydrocarbon chain-length increases.

Prof. A. R. Ubbelohde (*Belfast*) said: With regard to the papers of Hinshelwood and colleagues, it is not evident that we can dismiss the role of vibrational energy in determining the effect of the size of the molecule on the course of hydrocarbon oxidation, without careful consideration. Vibrational energy does not necessarily affect pyrolysis in the same way as it affects oxidations. It must be remembered that the controlling steps need not be the same in these reactions. Pyrolysis probably involves the breakage of a C—C link. In the case of oxidation of hydrocarbons the attack appears to predominate at the *end* of the molecule and probably involves activation of a C—H link in the first instance. Hydrocarbon oxidation involves a number of steps which might be controlled by the vibrational energy of the hydrocarbon molecules. By way of illustration we can consider three of these.

(1) *Initiation*—i.e. formation of a free hydrocarbon radical by removal of a H atom:

$$R—CH_3 + X \longrightarrow R—CH_2— + XH;$$

X may be an O_2 molecule but other molecules or radicals may also be effective in certain cases.

(2) "*Quantum-smudging.*"

$$R—CH_2— + O_2 \longrightarrow R—CH_2—O—O—.$$

The "molecule" formed in this process will not normally be strictly quantised and will fly apart after a greater or lesser interval unless it is stabilised by collisions in the meantime.

(3) *Chain branching* by breaking O—O link in peroxides, e.g.

$$R—CH_2—O|—OH \longrightarrow R—CH_2—O + OH.$$

With regard to the effect of vibrational energy on these three steps, the general factor to be considered is that, if we start with ethane as the simplest representative of the *n*-paraffins, and increase the chain length by attaching methylene groups, we shall thereby introduce the possibility of coupled vibrations in the molecule with frequencies of lower wave number than the ethane C—C vibration.[25] These vibrations extend throughout the carbon chain, but the coupling of additional methylene groups will not necessarily have much effect on C—H vibrations because of the difference in frequencies between C—C and C—H. Thus increasing the general length of the molecule and thereby lowering the wave number of the lowest vibrational frequency may be expected to influence primarily the reaction steps which involve these frequencies. The first step above, which involves a C—H bond activation, will probably not be very largely affected.

The second step, "quantum-smudging", will be favoured by an increased range of vibrational frequencies. The feature here is the temporary existence of an incompletely quantised molecule formed by binary collisions. Broadly speaking, the more frequencies available in the molecule, the longer the life before it breaks up again.

With regard to the third step, if the vibrational frequency of the O—O bond is sufficiently close to those of the hydrocarbon chain, the coupling of the O—O bond with these vibrations generally will facilitate activation involving the breaking of this bond. But if it differs substantially, the

[25] Cf. Ubbelohde, *Proc. Roy. Soc. A*, 1935, 152, 363, and published data on infra-red and Raman spectra.

O—O bridge will act like a double bond [26] which will not allow the vibrations to pass freely across it. Measurements of the activation energy involved in the pyrolysis of *n*-dialkyl peroxides should give useful information on this point.

Dr. P. Goldfinger (*Brussels* and *Nancy*) said : It seems not to have been sufficiently emphasised that Mr. Partington has found 98 % inhibition of the pyrolysis of ethane and 87 % in the case of propane. These seem to be about the highest figures reported hitherto on NO inhibition. We must admit therefore, that *at least* some part of these reactions follows a chain mechanism. Now in the case of butane Steacie [27] has argued that since the composition of the pyrolysis products, within the limits of error, are the same for the inhibited and uninhibited reaction, it is difficult to conceive two different mechanisms for them. The analysis of the decomposition products of the inhibited and uninhibited reactions in different cases will be therefore of great interest. It is conceivable that a partly inhibited chain reaction would give different products from those of an uninhibited reaction but it would be difficult to understand how the same products could originate from different mechanisms.

On the other hand according to Partington [28] the order of the reaction for *n*-hexane (at 530° c., from 25 to 220 mm.) and for cyclohexane (at 550° c., from 25 to 215 mm.) is 1·0 in the absence, and 1·5 in the presence, of NO. This is exactly what must be expected from Rice-Herzfeld-type mechanisms, as may be seen from general schemes worked out by Goldfinger, Letort and Niclause,[29] for a chain reaction in which the principal chain rupture is a collision of two radicals with a third body, which is in one case the primary product (first order) and in the other, an added substance as NO (1·5th order).

Dr. C. H. Bamford (*Maidenhead*) said : Unpublished experiments by Mrs. Bamford have shown that when mixtures of hydrogen, mercury vapour, and propylene are irradiated by mercury resonance radiation the following reactions occur :

$$Hg\ (6^3P) + H_2 \rightarrow 2H + Hg\ (6^1S) \quad . \quad . \quad . \quad (1)$$
$$H + C_3H_6 \rightarrow C_3H_7 \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$C_3H_7 + Hg \rightleftharpoons C_3H_7Hg \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The equilibrium in (3) lies well over to the right at 20° c. The attack of propyl radicals on mercury will be a very serious disturbing factor in Robb and Melville's experiments, since the removal of mercury atoms will reduce the rate of formation of atomic hydrogen. That there is in fact a large decrease in the concentration of free mercury atoms on the admission of small quantities of propylene to an irradiated mixture of hydrogen and mercury is shown by the following figures. The % absorption of 2537 A. is an indication of the concentration of mercury vapour.

(C_3H_6), mm.	% Absorption.
0	29·8
0·025	19·0
0·25	8·5
1·75	4·6

Incident intensity : $1{\cdot}55 \times 10^{14}$ quanta/cm².⁄sec
Initial (Hg) : 5×10^{-4} mm.
(H_2) : 10 mm.

Thus the addition of 0·25 mm. C_3H_6 is sufficient to cut down the rate of production of hydrogen atoms by a factor of 3·5. In Robb and Melville's experiments the times taken in a typical run for the MoO_3 to reach a standard blueness were in the ratio 2 : 1 (with and without C_3H_6). It

[26] Ubbelohde, *loc. cit.*, p. 368.
[27] *Atomic and Free Radical Reactions* (New York, 1946).
[28] Private communication.
[29] *V. Henri Memorial Vol.* (Liége) (in press).

is clear that the above effect alone is capable of accounting for a good deal of this, and the calculated velocity constants are too high.

The presence of liquid mercury in the reaction vessel was found to have little effect, on account of the slow diffusion of the vapour.

Prof. H. W. Melville and Mr. J. C. Robb (*Aberdeen*) (*communicated*): In reply to Dr. Bamford, who suggests that the observed diminution in hydrogen atom concentration in presence of added propylene is due to a reversible reaction,

$$Hg + C_3H_7 \rightleftharpoons Hg\,C_3H_7,$$

reducing the rate of generation of atomic hydrogen and that no hydrogenation of the propylene occurs, we wish to make the following observations although his experimental methods and results are at the moment unpublished and unknown to us. We can thus make no comment on his results.

Referring to our paper, it is shown in Tables II and III that estimates of the collision efficiency of the reaction

$$H + C_3H_6 \rightarrow C_3H_7$$

agree well although measured in two different ways. Table III gives results based on the amount of atomic hydrogen reaching the molybdenum oxide plate (*a*) in absence of propylene and (*b*) in presence of propylene. Table II is based, on the other hand, on the actual number of propylene molecules hydrogenated in the system. This entirely disproves the above criticism and it can be said with certainty that the hydrogen atoms are utilised in a hydrogenation reaction.

However, the point raised by Bamford is not entirely without interest since we have observed that in a system containing a limited amount of mercury, a clean-up of the mercury vapour is eventually accomplished by butyl radicals and it seems to us that this clean-up is probably due to the formation of the mercury dialkyl, although the concentration of the dialkyl would be so low as to make its detection practically impossible. The reaction products have a smell rather characteristic of mercury dialkyls.

We wish to take this opportunity to suggest an explanation of a phenomenon reported by Vanhaeren and Jungers.[30] In their investigations on the hydrogenation of ethylene and propylene photosensitised by mercury vapour, it is reported that at room temperature and in presence of only a saturation pressure of mercury vapour, the reaction of hydrogen atoms with the olefine is much slower than at higher temperatures. Further, if mercury vapour is present in the reaction vessel and also liquid mercury, then the rate at low temperatures and high temperatures is the same. We would suggest the following explanation.

The equilibrium reactions mentioned above occur at low temperatures, the complex formed becoming more unstable at higher temperatures, thus accounting for the slower rate of reaction at low temperatures by the mercury vapour removed. When liquid mercury is present, however, the normal rate conditions are restored since the rate of evaporation of mercury from the droplets is quite sufficient to maintain the normal saturated vapour pressure.

In all our experiments, liquid mercury was present and the pressures employed by us were very much lower than those in the paper quoted, and diffusion effects of mercury would be negligible. Further, it is a feature of our investigations that only a very low quantum input is required to the reaction vessel and the stationary concentrations of atomic hydrogen and free alkyl radicals is so low that the amount of mercury which could be removed by such an equilibrium would be very small.

Dr. C. H. Bamford (*Maidenhead*) (*communicated*): Prof. Melville and Mr. Robb have missed the point of my remarks in the first part of their

[30] *Bull. Soc. Chim. Belg.*, 1945, **54**, 236.

statement. I did not suggest that "no hydrogenation of propylene by hydrogen atoms occurs" in their experiments, since the formation of propyl radicals from propylene is a hydrogenation (eqn. (2)). My point was that when propylene is added to an irradiated mixture of hydrogen and mercury vapour the stationary concentration of hydrogen atoms falls for two reasons: (1) the reaction between hydrogen atoms and the olefine, and (2) the attack of the resulting radicals on mercury, which results in a reduction of the quantum input, and the rate of formation of hydrogen atoms. In our experience, (2) is at least as important as (1) under conditions similar to Robb and Melville's. The sum of the two effects is measured in their experiments. The agreement between the results in Tables II and III in Robb and Melville's paper is not significant, and has no bearing on my original criticism. In both cases the quantum input as measured in the absence of olefine was too high.

The results of Vanhaeren and Jungers certainly show that when liquid mercury is present and suitably distributed over the walls of the reaction vessel, sufficient vapour is present (not necessarily uniformly distributed) to absorb most of the incident light. On the other hand, our results indicate that when liquid mercury is present only in the lower portion of the vessel the rate of evaporation is not great enough to maintain saturation pressure. Melville and Robb's results are significant only if their reaction vessel contained a uniform pressure of mercury vapour. Whether or not this was so depends on the distribution of liquids in the vessel. Since there is no mention in the original paper of the presence of liquid mercury it is not profitable to discuss the matter further.

Dr. C. A. McDowell and Mr. J. H. Thomas (*Liverpool*) (*communicated*): We should like to mention that our recent investigation of the low-temperature oxidation of gaseous acetaldehyde when peractetic acid is the main product, leads us to postulate an initiation process which is analogous to that put forward by Prof. Hinshelwood and his collaborators, namely,

$$CH_3CHO + O_2 \longrightarrow CH_3 . CO^\bullet + HO_2 \quad . \quad . \quad . \quad (1)$$

$$CH_3CO^\bullet + O_2 \longrightarrow CH_3 . C\genfrac{}{}{0pt}{}{\diagup OO^\bullet}{\diagdown O} \quad . \quad . \quad . \quad (2)$$

$$CH_3 . C\genfrac{}{}{0pt}{}{\diagup OO^\bullet}{\diagdown O} + CH_3 . CHO \longrightarrow CH_3 . C\genfrac{}{}{0pt}{}{\diagup OOH}{\diagdown O} + CH_3 . CO^\bullet \quad . \quad (3)$$

B.—OTHER RADICALS.

THE EXISTENCE OF THE RADICAL HO_2 IN THE GAS PHASE.

By G. J. Minkoff.

Received 30*th July*, 1947.

Since Haber [1] first suggested that the radical HO_2 might be involved in the reaction between hydrogen and oxygen, HO_2 has been postulated as an intermediate in many gas-phase reactions. The existence of the radical is supported by considerable chemical evidence and by some theoretical discussion (see, e.g. Hinshelwood and Williamson,[2] Bates,[3]

[1] Haber, *Naturwiss.*, 1931, **19**, 450.

[2] Hinshelwood and Williamson, *The Reaction between Hydrogen and Oxygen* (Oxford, 1934).

[3] Bates, *J. Chem. Physics*, 1933, **1**, 457; *Z. physik. Chem.*, *B*, 1933, **22**, 469.

Kassel,[4] Weiss,[5] and Gaydon [6]). The physical evidence is negligible. In this communication, it is intended to review briefly the chemical evidence and to present some theoretical support for the existence of HO_2.

The reaction between hydrogen and oxygen in the presence of u.-v. light (whether sensitised by mercury or not), was shown by Bates and Salley [7] to lead almost exclusively to the formation of H_2O_2; this confirmed the mechanisms of Marshall [8] and of Kistiakowsky,[9] who had found quantum yields > 1 in similar investigations. The chain reactions postulated were

$$H + O_2 \rightarrow HO_2$$
$$HO_2 + H_2 \rightarrow H_2O_2 + H.$$

In view of later work (see below) the first reaction should be modified to include collision with a third-body, except in special circumstances. For conditions near to room temperature and pressure, the second reaction is open to some doubt, since in the thermal combination of hydrogen and oxygen (above 450° c.), the second pressure limit is explained in terms of the removal of the chain-carrying hydrogen atoms by their association with oxygen molecules. The further reactions of the HO_2 so formed are not sufficiently rapid for the explosion-chain to be continued. This is in marked contrast to the photochemical reaction in which (according to Bates' scheme), practically every HO_2 should react with H_2 to give H_2O_2. Smith and Napravnik [10] have pointed out that the reaction is energetically improbable at room temperature, and suggest

$$2HO_2 \rightarrow H_2O_2 + O_2$$

as an alternative mechanism. The reaction

$$HO_2 + H \rightarrow H_2O_2$$

may also be important, if the energy of this reaction is removed by collision before the peroxide is disrupted.

The gas-phase reaction of hydrogen and oxygen above 400° c. provides stronger evidence for the existence of HO_2. The low-pressure explosion of mixtures of hydrogen and oxygen is described by the following chain mechanism: [11]

$$H + O_2 \rightarrow OH + O,$$
$$O + H_2 \rightarrow OH + H,$$
$$OH + H_2 \rightarrow H_2O + H.$$

When the pressure is above a critical value, the gas mixture no longer explodes, but reacts at a measurable rate. There is much evidence for believing that this phenomenon is due to the number of H atoms which react with oxygen molecules in termolecular collisions. The HO_2 radicals so formed react too slowly to continue the explosion chain. The HO_2 radicals can be destroyed on the vessel walls or they can react with one another or with hydrogen. Most of the known experimental facts relating to the hydrogen-oxygen reaction have been explained on the basis of the above scheme by Hinshelwood [11] and by Lewis and von Elbe.[11]

Geib and Harteck [12] have studied the reaction of hydrogen atoms with

[4] Kassel, *Annual Survey of American Chemistry*, VIII (N.Y., 1933), p. 27.

[5] Weiss, *Trans. Faraday Soc.*, 1935, **31**, 668.

[6] Gaydon, *Spectroscopy and Combustion Theory* (Chapman and Hall, 1942), p. 112.

[7] Bates and Salley, *J. Amer. Chem. Soc.*, 1933, **55**, 110.

[8] Marshall, *J. Physic. Chem.*, 1926, **30**, 34, 1078; *J. Amer. Chem. Soc.*, 1932, **54**, 4460.

[9] Kistiakowsky, *ibid.*, 1930, **52**, 1868.

[10] Smith and Napravnik, *ibid.*, 1940, **62**, 385.

[11] Hinshelwood, *Proc. Roy. Soc., A*, 1946, **188**, 1; Lewis and von Elbe, *J. Chem. Physics*, 1942, **10**, 366.

[12] Geib and Harteck, *Ber.*, 1932, **65**, 1551.

oxygen molecules at low temperatures and pressures. As the temperature of reaction decreased, so the product tended more nearly to 100 % H_2O_2. This was explained by the effect of the lower temperature which favoured the termolecular processes:

$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + H + M \rightarrow H_2O_2 + M,$$

against the bimolecular exchange reaction

$$H + O_2 \rightarrow OH + O,$$

which requires more activation energy. Farkas and Sachsse [13] studied the recombination of hydrogen atoms; they found that at pressures above 200 mm., their results were consistent with the hypothesis that H atoms reacted with O_2 to give HO_2 in termolecular collisions. Rodebush [14] reached a similar conclusion as a result of work on the reactions of hydrogen atoms with oxygen at much lower pressures; under these conditions, the bimolecular exchange reaction, $H + O_2 \rightarrow OH + O$, was the more important. The reaction of hydrogen with chlorine was found by Bodenstein and Schenk [15] to be inhibited by oxygen. Their results were said to indicate that this inhibition was due to removal of H atoms by O_2, and that the HO_2 radicals were formed in termolecular collisions. Kassel [4] suggested in 1933 that their evidence was not conclusive, and referred to the work of Norrish and Ritchie.[16] These authors investigated the problem more fully than did Bodenstein and Schenk; they derived expressions in good agreement with their experimental results relating quantum yields to concentrations of the reactants. Their reaction mechanism involved the formation of HO_2 in bimolecular collisions. Closer inspection shows that their results are also satisfactorily interpreted by a mechanism according to which the HO_2 is formed in termolecular reactions. This is supported by the work of Rodebush and Klingenhoefer,[17] who found that at low pressure, oxygen had no effect on the quantum yield. This is in accord with the view that under these conditions, termolecular collisions are very rare, so that the reaction,

$$H + O_2 + M \rightarrow HO_2 + M,$$

would no longer be efficient in reducing the quantum yield. Ritchie [18] later showed that the reaction was termolecular; he also investigated the effects of different inert gases in stabilising HO_2.

Studies of the photo-oxidation of HI have also yielded information regarding the radical HO_2. Kondratiew and Kondratiewa [19] showed that the reaction proceeded through the formation of HO_2, which subsequently oxidised the HI. They pointed out that the radical need not dissociate immediately through retaining its energy of formation if this energy could be shared with vibrational degrees of freedom. Cook and Bates [20] obtained evidence from studies of the kinetic progress of the oxidation of HI which enabled a decision to be made as to whether the formation of HO_2 (at pressures above 15 cm.) was due to bi- or ter-molecular. reactions. The results showed that the reaction was in fact termolecular, The reaction appeared to proceed in approximately one out of two, or three, collisions, which suggested a low activation energy, in good agreement with the results of Bodenstein and Schenk [15] and of Farkas and Sachsse.[13] Bates calculated that the lifetime of the HO_2 was of the order of 10^{-8} sec.

[13] Farkas and Sachsse, *Z. Physik. Chem.*, *B*, 1934, **27**, 111.
[14] Rodebush, *J. Physic. Chem.*, 1937, 41, 283.
[15] Bodenstein and Schenk, *Z. Physik. Chem.*, *B*, 1933, **20**, 420.
[16] Norrish and Ritchie, *Proc. Roy. Soc.*, *A*, 1933, **140**, 713.
[17] Rodebush and Klingenhoefer, *J. Amer. Chem. Soc.*, 1933, **55**, 130.
[18] Ritchie, *J. Chem. Soc.*, 1937, 857.
[19] Kondratiew and Kondratiewa, *J. Physic. Chem.*, *U.R.S.S.*, 1934, **5**, 1411.
[20] Cook and Bates, *J. Amer. Chem. Soc.*, 1935, **57**, 1775.

Physical evidence for the existence of HO_2 is very meagre. Chara [21] claims that after water vapour had been passed through an electrodeless discharge and then into a trap at − 180° c., the solid product obtained had a formula of H_2O_4. This result does not agree with that of Campbell and Rodebush,[22] who found, in similar experiments, that the products were H_2O and H_2O_2. Eisenhut [23] applied the mass-spectrographic technique to a mixture of CH_4 and oxygen. Amongst other lines, a faint line appeared which Hinshelwood and Williamson [8] ascribed to HO_2. The line, however, corresponds to a mass of 34, and so is probably due to $O^{16}O^{18}$, rather than to HO_2, which has a mass of 33. No spectroscopic data has yet been reported which indicates the existence of HO_2. This may possibly be due, not to the absence of HO_2, but either to the fact that its concentration may be too small to be detected spectroscopically, or that its spectrum is situated unfavourably for observation.

It was at one time believed that the product of a bimolecular association would decompose unless collision occurred with some molecule which would remove a large part of the energy of formation of the new molecule. This energy would otherwise cause violent vibration, and eventual rupture, of the newly-formed bond. However, as Kassel [24] pointed out in 1931, the time before rupture occurred could be increased to some extent if the energy of formation was shared with other vibrational degrees of freedom. The lifetime of the new molecule might now be sufficient for the molecule to collide with another molecule, and so become stabilised through the loss of some of the energy of formation. An actual illustration of the effect is provided by the following step in the oxidation of a hydrocarbon RH (R being an aliphatic radical) :

$$R— + O \rightarrow R—O—O—.$$

Early work on the oxidation of higher hydrocarbons by Egerton and Pidgeon [25] and others had led to the peroxidation view of the combustion process, as a result of which Ubbelohde [26] first postulated the mechanism involving the radical RO_2. The large number of vibrational degrees of freedom in this radical can accommodate most of the energy of formation ; the reaction can therefore occur as a bimolecular process sufficiently frequently to have been generally accepted as an essential step in the reaction mechanism (see, e.g. George and Rideal,[27] and Walsh [28]).

The problem was considered in the light of the quantum theory by Rosen,[29] at the suggestion of Prof. Bates. By making certain assumptions (amongst them, a linear structure of the radical), Rosen was able to show that an HO_2 molecule formed by a bimolecular association would be stabilised by the conversion of the energy of formation into vibrational energy. He calculated that if a certain vibrational quantum number of the molecule had values 1, 2, 3 or 4, the corresponding lifetimes of the molecule would be of the order of 5×10^{-15}, 5×10^{-13}, 5×10^{-11}, or $2{\cdot}5 \times 10^{-9}$ sec. respectively. Experimental evidence has recently been obtained by Egerton and Minkoff,[30] which supports the above conclusions. Hydrogen peroxide was obtained in low-pressure explosions of hydrogen-oxygen mixtures. A part of this peroxide was formed on the cooled walls (at − 180° c.) by the recombination of OH radicals ; the remainder was formed in the gas phase, whether the walls were cooled or not. The yield

[21] Chara, *J. Chem. Soc., Japan*, 1940, **61**, 569.
[22] Campbell and Rodebush, *J. Chem. Physics*, 1936, **4**, 293.
[23] Eisenhut, *Z. Elektrochem.*, 1930, **36**, 656.
[24] Kassel, *J. Amer. Chem. Soc.*, 1931, **53**, 2143.
[25] Egerton and Pidgeon, *Proc. Roy. Soc., A*, 1933, **142**, 26.
[26] Ubbelohde, *ibid.*, 1935, **152**, 354.
[27] George and Rideal, *ibid.*, 1946, **185**, 288.
[28] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 269.
[29] Rosen, *J. Chem. Physics*, 1933, **1**, 319.
[30] Egerton and Minkoff, *Proc. Roy. Soc., A* (in press).

of peroxide was a maximum at a pressure of 4 cm. Hg, and decreased when the pressure was either increased or decreased. There seemed only one way of explaining these results without contradicting the established theories of the hydrogen-oxygen reaction outlined above. At very low pressures, the time between collisions is greater than the lifetime of unstabilised HO_2; at such pressures, there will effectively be no HO_2 present, and no peroxide will be formed. At rather higher pressures, collisions are more frequent, and the time between them may now be such that the HO_2 radical (stabilised according to the above process) undergoes several collisions in the course of its calculated lifetime. The HO_2 retains its energy of formation, and can use this, in collisions with H_2, for the reaction

$$HO_2 + H_2 \rightarrow H_2O_2 + H$$

to occur frequently. The peroxide carries off some of the energy, and decomposes unless it is frozen on cold walls. The infra-red spectrum is shortly to be investigated in order to find, amongst other information, whether the peroxide carries off this energy as vibrational energy. At higher pressures still, when the HO_2 is formed mainly in termolecular collisions and does not possess its energy of formation, it can only react infrequently with H_2, so that the yield of peroxide is smaller.

Dainton and Norrish [31] studied the more complex problem of the explosions of hydrogen-oxygen mixtures sensitised by NO_2. Their results led them to suggest tentatively that NO_2 may be dissociated to NO and O when it reacts with an HO_2 radical which has retained its energy of formation, though they did not discuss how the HO_2 retained its energy of formation.

Information from Potential Energy Surfaces.

Some information regarding the existence of HO_2 should arise from a study of the change of the energy of the system H . . O . . O as it passes from the configuration $H + O_2$ to $HO + O$. A semi-empirical method of treating such a problem has been developed by Glasstone, Laidler, and Eyring.[32]

If the coulombic (attractive) forces between the atoms X and Y, Y and Z, and Z and X are represented by A, B and C respectively, and if α, β and γ represent the energy terms due to exchange forces, then the energy E of the system is given by the Heitler-London equation (assuming the bonding electrons to be s-electrons)

$$E = A + B + C - [\tfrac{1}{2}\{(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2\}]^{\frac{1}{2}}.$$

For each pair of atoms, the sum of coulombic and exchange energy is equal to the potential energy of the pair of atoms. This can be obtained directly, for various interatomic distances, from the well-known Morse curves, which are derived from spectroscopic data (energy of dissociation, vibration frequencies, and molecular dimensions). The ratio of coulombic to potential energy is obtained with the aid of rules derived by Glasstone *et al.* When the principal quantum number n of the bonding electrons is 1, the coulombic energy is taken as 12 % of the potential energy; it is 22 % when $n = 2$, and 32 % when $n = 3$. When p-electrons are involved, the coulombic energy is much more important.[33] It is assumed that the percentage of coulombic energy is independent of the distance between the atoms; this is only an approximation, and it is one of the weaknesses of the method.

The energy E of the system X . . Y . . Z is then calculated for various interatomic distances, and a contour map is drawn relating points

[31] Dainton and Norrish, *Proc. Roy. Soc., A*, 1940, 177, 445.
[32] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw Hill, 1941).
[33] Bartlett, *Physic. Rev.*, 1931, 37, 507.

of equal energy with the configuration. This is the potential energy surface. The path followed by the reacting system is that of lowest energy, and usually involves a smooth rise to a maximum (representing the transition state), followed by a smooth decrease. A "potential hollow" is sometimes found at the top of the reaction path. Although it is possible that it is caused by a defect in the method, such a hollow probably represents a transition state of comparative stability. In general, many useful results have been obtained by the application of the method, usually in fairly good agreement with experimental data. The limitations of the method have been discussed by James and Coolidge.[34]

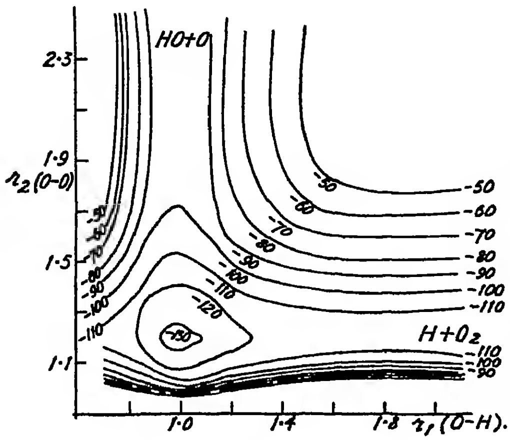

FIG. 1.

It is inherent in the method that a linear configuration of the transition state has the lowest energy, though possibly this may not be the true shape of HO_2. However, as shown below, the vibration frequencies of the linear HO_2 can be calculated, and these should assist in deciding the structure if the vibration spectrum of the radical should be observed experimentally. The results obtained in the present investigation will probably be little affected by treating the bonding electrons as *s*-electrons, when in fact the *p*-electrons of oxygen are involved. Several problems have been similarly treated by Glasstone *et al.* in connection with reactions of hydrocarbons and of halogens, with satisfactory results. The reaction, $H+HCl \rightarrow H_2+Cl$ has been treated by Steiner and Rideal,[35] assuming a linear configuration, *s*-electrons, and 20 % coulombic energy. They found a deep hollow at the transition state, 25 kcal. stable with respect to the energy maximum. A less empirical, but much more complicated, calculation of the problem by Magee,[36] who used the perturbation method, showed that when the electrons are considered as two *s*- and one *p*-electrons, a triangular H_2Cl was formed which was 30 kcal. stable, while a corresponding linear complex was 15 kcal. stable.

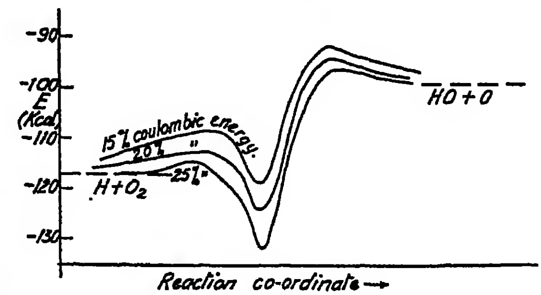

FIG. 2.

Potential energy surfaces have been calculated for the system H . . O . . O, assuming 15, 20 and 25 % coulombic energy. The surface for 25 % is shown in Fig. 1, while Fig. 2 shows the change of energy

[34] James and Coolidge, *J. Chem. Physics*, 1933, 1, 825.
[35] Steiner and Rideal, *Proc. Roy. Soc.*, *A*, 1939, 173, 503.
[36] Magee, *J. Chem. Physics*, 1940, 8, 677.

with reaction co-ordinate for the different values of the coulombic energy As H approaches O_2, the energy rises slightly, then falls by 21 kcal. For the remainder of this discussion, 20 % coulombic energy will be assumed, though this value may well be low (Haber, Heitler and Weiss,[37] in calculations of the stability of HO_2, assumed 33 % coulombic energy).

The potential energy surfaces thus show that HO_2 can be formed from H and O_2, only a small activation energy being required. If a third-body removes some of the energy of formation, the radical no longer possesses the activation energy necessary for its dissociation, and it should then be stable. It is also seen that when the reacting entities possess sufficient energy, the system will pass from HO_2 to HO + O unless energy is removed by a third-body before the system passes over the high potential barrier. These considerations are in agreement with the conclusions of Bates and of Bodenstein and Schenk, that the formation of HO_2 in termolecular processes has a low activation energy.

The force constants and vibration frequencies of the linear HO_2 were calculated from the potential energy surfaces by the methods described by Glasstone *et al.* The parallel force-constants, f_{11}, f_{12} and f_{22}, were obtained from the equation

$$E-E^{\circ}=\tfrac{1}{2}f_{11}(r_1-r_1^{\circ})^2+f_{12}(r_1-r_1^{\circ})(r_2-r_2^{\circ})+\tfrac{1}{2}f_{22}(r_2-r_2^{\circ})^2$$

where the superscript ° refers to the bottom of the hollow, and r_1 and r_2 are the H . . . O and O . . . O distances respectively. The bending-force constant f_ϕ was obtained from the expression:

$$E - E^{\circ} = \tfrac{1}{2}r_1^{\circ}r^{\circ}_2 f_\phi \, . \, \phi^2$$

where ϕ is the angle of deformation. The values obtained were

$f_{11} = 4{\cdot}0 \times 10^5$ dynes. cm.$^{-1}$; $f_{22} = 8{\cdot}7 \times 10^5$ dynes. cm.$^{-1}$;
$f_{12} = 1{\cdot}5 \times 10^4$ dynes. cm.$^{-1}$; $f_\phi = 4{\cdot}0 \times 10^3$ dynes. cm.$^{-1}$.

The vibration frequencies were then found to be 1300 cm.$^{-1}$ and 2900 cm.$^{-1}$ for the parallel vibrations, and 320 cm.$^{-1}$ for the bending vibration. These values are necessarily approximate; they are not materially affected when 25 % instead of 20 % coulombic energy is used. Comparison with the frequencies of HCN (2089, 3312, 712),[38] a linear molecule of similar dimensions, shows that the values are of the right order of magnitude. The smaller values for HO_2 may indicate weaker binding forces. This is especially noticeable for the bending vibration; large distortions may occur with but slight changes in energy. This is interesting when it is remembered that if HO_2 is formed by the removal of an H atom from H_2O_2, which has a skew structure with the H—O—O angle approximately 100°,[39] a linear structure would not be expected. Further, an isosceles triangular HO_2 might be considered as participating to some extent in the structure of HO_2, since it would be stabilised by resonance of the OH bond between the two equivalent O atoms.

If HO_2 possessed a stable excited electronic state, which was suitably situated, it should be possible to observe spectroscopically the electronic transitions. At the suggestion of Dr. Gaydon, the existence of the upper state was investigated by calculating potential energy surfaces for systems in which the initial state was H(^2S) (i.e. ground state), together with O_2 in the lowest electronic state which would normally dissociate into an excited O atom in the (^1D) state, and one in the ground state. In one set of calculations, the products were assumed to be O in the ground state and OH in the excited ($^2\pi$) state, while in the other set of calculations the products were taken to be OH in the ground state and excited O (^1D). It was found that in the second set, reaction did not seem to be possible; in the first set, reaction took place, and a hollow appeared at the transition

[37] Haber, Heitler and Weiss (private communication).
[38] Herzberg, *Infra-Red and Raman Spectra* (van Nostrand, 1945).
[39] Penney and Sutherland, *J. Chem. Physics*, 1934, **2**, 492.

state, corresponding to HO_2. The H—O and O—O bond lengths were then 1·0 and 1·4 A. respectively. The separation of the two energy minima was 100 kcal., corresponding to an electronic transition at 2900 A.

In view of the limitations of the method, the evidence provided by the potential energy surfaces cannot be claimed to be compelling evidence for HO_2. It was nevertheless interesting to find out whether or not the method would support the postulated existence of HO_2. The general conclusion is at least in accord with the chemical evidence; further confirmation of the stability of HO_2 is provided in an extensive discussion of the thermo-chemistry of the radical by Walsh.[40]

The author wishes to thank Prof. Sir A. C. Egerton, Dr. A. G. Gaydon, and Mr. A. McColl for many helpful discussions; and Mr. A. J. Everett for photographing and enlarging the mass spectrographs in the paper by Eisenhut.[23]

Summary.

The chemical evidence for the formation of HO_2 in the gas-phase is briefly reviewed, and the question of whether HO_2 is formed in bimolecular or termolecular collisions is discussed in the light of recent work by Egerton and Minkoff.* The conclusion to be drawn is that as the pressure is increased, so the reaction proceeds by termolecular rather than bimolecular collisions. In an intermediate range of pressures, HO_2 can undergo certain reactions when it still possesses its energy of formation. In the present communication, the semi-empirical method of Glasstone, Laidler, and Eyring,† has been applied to the reaction $H + O_2 \rightarrow HO + O$; a deep trough, which may indicate the existence of HO_2 has been found at the transition state, when a linear configuration is assumed. Possible vibrational and electronic frequencies of such a linear complex are calculated.

Résumé.

On passe en revue les preuves chimiques de la formation de HO_2 en phase gazeuse et on conclut que sa formation se poursuit par des chocs trimoléculaires quand la pression est accrue. Des calculs semi-empiriques ont été faits pour la réaction $H + O_2 \rightarrow HO + O$; ils indiquent qu'il est possible de trouver HO_2 linéaire à l'état de transition. On a calculé ses fréquences électroniques possibles et celles de vibration.

Zusammenfassung.

Es wird eine Übersicht über die chemischen Beweise, die für die Bildung von HO_2 in der Gasphase bestehen, gegeben und es wird geschlossen, dass bei Steigerung des Drucks die Bildung durch termolekulare Stösse erfolgt. Halbempirische Berechnungen sind für die Reaktion

$$H + O_2 \rightarrow HO + O$$

durchgeführt worden und zeigen, dass es möglich ist, dass ein geradliniges HO_2 am Übergangszustand vorgefunden werden kann. Die möglichen Kernschwingungs- und Elektronenfrequenzen sind berechnet worden.

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Imperial College,
S.W.7.

[40] Walsh, *J. Chem. Soc.* (in press).

* *Proc. Roy. Soc. A* (in press).

† *The Theory of Rate Processes* (1941), McGraw Hill.

RADICAL SPECTRA IN FLUORESCENCE.

By P. J. Dyne and D. W. G. Style.

Received 28th July, 1947.

Although the band spectra of a large number of diatomic radicals are well known, examples of polyatomic radical spectra are rare. In fact the only known examples are, with their presumed emitters, the hydrocarbon flame bands (HCO),[1] the α-ammonia band (NH_2),[2] and the comet-tail band at 4051 A. (CH_2),[3] to which should perhaps be added a system obtained as a fluorescence from HCOOH vapour, and which has been tentatively assigned to HCO by Terenin and Neujmin.[4]

Photo-dissociation of a polyatomic molecule may lead to the primary formation of stable molecules, two radicals, or an atom and a radical. With light of high-enough frequency one or other of the products may be electronically excited, and under favourable conditions the excitation energy may be emitted as a fluorescence. Such radical fluorescence spectra have been observed with a number of diatomic radicals [5] and with NH_2.[1] By using exciting radiation of known frequency estimates have been made of the energy required to rupture certain bonds.[6]

A few results obtained with some simple carbonyl compounds are now reported. The fluorescence was excited by a low-tension arc in H_2 constructed, with minor modifications, after the design of Allen.[7] The discharge passed through a hole in a copper diaphragm and the Cu resonance lines at 3274 and 3247 A. were rather prominent in the spectrum which was recorded by a quartz spectrograph. Light from the arc passed through a fluorite window into the fluorescence chamber. Any fluorescence emerged at right angles to the exciting beam through a quartz window and was focussed onto the slit of a f. 8 spectrograph with a dispersion of *ca.* 50 A./mm. at 3000 A. The arc was run from a 110 V. supply at 5 amp. During an exposure the vapour under examination was distilled continuously through the fluorescence chamber.

The transparency of the fluorite window was regularly checked by observation of the intensity of the OH bands emitted by H_2O vapour when illuminated by the arc. The 3064 A. band could be detected on Kodak 0·800 plates with exposures of a few minutes, while with B·20 process plates and a narrow slit the head of this band is much over-exposed and the 2811 A. band appears weakly. If the processes responsible for this emission are:

$$H_2O + h\nu_1 \longrightarrow H + OH^*$$

and

$$OH^* \longrightarrow OH + h\nu_2$$

the wavelengths required to excite the OH bands are respectively *ca.* 1345 and 1295 A. The emission of the arc is fairly strong near the first wavelength but is weak in the region of the latter.

With the fairly wide slit (0·025 mm. on the photographic plate), used to obtain the spectra to be described, no emission was detectable with CH_3CHO, either visually, or with exposures of up to 6 hr.

Formaldehyde, at a pressure of a few tenths mm. Hg., gave no visible fluorescence, but bands were discernible on the plate with an exposure of 1 hr., and fairly good exposures were obtained in 6 hr. Longer exposures were not attempted as the fluorite window became covered with a film which was already nearly opaque to the exciting radiation after 4 hr. This film was not soluble

[1] Vaidya, *Proc. Roy. Soc., A*, 1934, 147, 513.
[2] Rimmer, *Proc. Roy. Soc., A*, 1923, 103, 696.
[3] Swings, *Rev. Mod. Physics*, 1942, 14, 195.
[4] *Acta. Physicochim.*, 1936, 5, 465.
[5] Popov, *Acta Physicochim.*, 1936, 4, 559.; Petrova, *ibid.*, 559; Terenin and Prileskjewa, *ibid.*; Jakobleva, *ibid.*, 1938, 9, 665, and 1939, 10, 439; Wieland, *Z. Physik.*, 1932, 76, 801, and 1932, 77, 157; also ref. 4 and 6.
[6] Wieland, *Z. physik. Chem. B*, 1939, 42, 422.
[7] Allen, *J. Opt. Soc. Amer.*, 1941, 31, 268.

in organic solvents, but was readily removed by Na_2CO_3 solution. The exciting wavelength probably lies below 1345 A., since on one occasion, when the window had been imperfectly cleaned, no bands were obtained with CH_2O, although well-developed OH bands were obtained with H_2O vapour. The bands are degraded towards the red (Fig. 1) and the wavelengths of all those that have been measured are listed in Table I, together with the wavelengths recorded by Vaidya for all " A " hydrocarbon flame bands between 4092 and 2858 A.[1]

TABLE I.

CHO Fluorescence.		Flame Bands.		v'.	v''.
λ(A.) (Vaidya).	Intensity.	λ(A.).	Intensity.		
4089	1	4092·0	3	1	12
3989	1	3987·5	2	0	11
3824	2	3824·9	4	1	11
3729	3	3730·5	5	0	10
—	—	3676·0	1	2	11
—	—	3635·6	3	A''	
3588	3	3588·6	8	1	10
—	—	3539·9	2	3	11
3504	4	3502·7	8	0	9
—	—	3458·4	1	2	10
3415	2	3417·4	3	A''	
3377	4	3377·4	10	1	9
3295	3	3299·2	10	0	8
3217	2	hidden by OH		A'' ?	
3185	3	,, ,,	,,	1	8
3114	3	,, ,,	,,	0	7
3040	1	,, ,,	,,	A'' ?	
3011	2	3014·8	8	1	7
2947	2	2948·2	7	0	6
2858	1	2858·0	6	1	6

The two systems are clearly identical. No " B " bands were observed in fluorescence, and, as might be expected from the lower temperature of the source, the fluorescent bands are narrower and have sharper heads. There can remain little doubt that the emitter is HCO.

The absorption spectrum of HCHO shows two diffuse bands at 1287 A. and 1223 A., together with others at shorter wavelengths, which are unlikely to be transmitted by fluorite.[3] The H_2 spectrum is very weak at 1287 A., but the 1223 A. absorption band is the weaker, and although it overlaps a H_2 emission band, the intensity of the latter may be very much reduced in passage through the fluorite window. Although Vaidya's v'' is uncertain his v' is probably correct. In fluorescence, bands with $v' > 1$ are absent, possibly because they are too weak. Accepting Vaidya's v'' and the real absence of bands with higher v', the heat of rupture of the H—CHO bond has a maximum value of 90 or 101 kcal., for active wavelengths of 1287 and 1223 A. respectively. Since the deformation vibration of the newly formed HCO radical would be expected to be strongly excited, the equilibrium value of the dissociation energy must be considerably less than these figures.

As already reported[4] HCOOH rapidly forms an opaque deposit on the window. It emits a weak blue fluorescence, which is strongly quenched by higher pressures and is of maximum intensity at a few tenths mm. Hg. The deposit differs from that formed by HCHO, being removed by acetone. Owing to the rapidity with which the window becomes opaque, only rather under-exposed plates have been obtained which show some 25

[3] Price, *J. Chem. Physics*, 1935, 3, 256

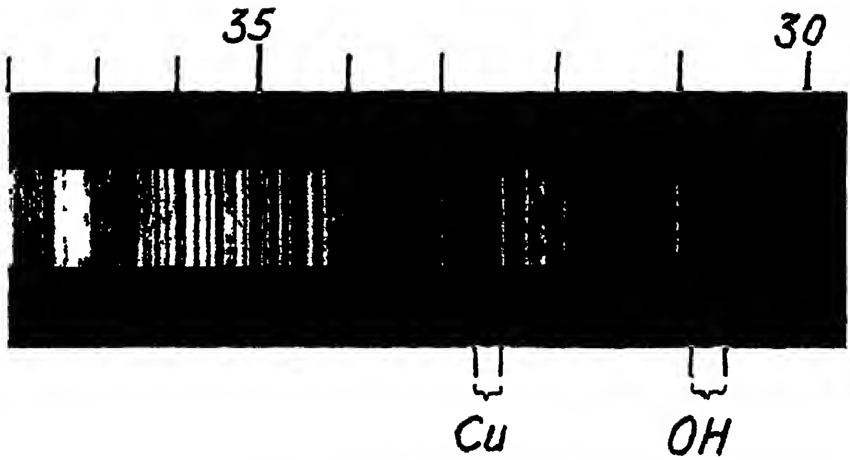

FIG. 1 —Part of fluorescence from HCHO Positive × 10.

[To face page 160.

bands between 4400 and 3400 A. and also the 3064 A. OH band. It has not been possible to measure up the plates with sufficient accuracy to justify tabulation of wavelengths, but in Fig. 2 the approximate wave-numbers and intensities are shown. For the emitter the choice lies between HCOOH, COOH and, as suggested by Terenin and Neujmin, HCO. The last seems improbable.

One of us (P. J. D.) wishes to acknowledge receipt of a grant from the Department of Scientific and Industrial Research.

FIG. 2.

Summary.

A fluorescent band system, excited in gaseous CH_2O by light in the fluorite region from a H_2 arc, is identified with the hydrocarbon flame system. A second system of uncertain origin is emitted by HCOOH when illuminated by the same source.

Résumé.

CH_2O gazeux, excité par la lumière d'un arc à hydrogène moléculaire dans la région de la fluorite, donne un spectre de bandes fluorescent, qui est identique a celui de la flamme d'hydrocarbure—H COOH, illuminé par la même source, émet un autre spectre d'origine incertaine.

Zusammenfassung.

Ein Fluoreszenzbandensystem in gasförmigem CH_2O durch das Licht in der Fluoritregion eines H_2-Bogens wird mit dem Wasserstofflammensystem identifiziert. Ein zweites System, dessen Ursache ungewiss ist, wird ausgegeben, wenn HCOOH mit derselben Quelle beleuchtet wird.

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FREE RADICALS IN LOW-PRESSURE FLAMES.

BY A. G. GAYDON AND H. G. WOLFHARD.

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It is well known that many free radicals, such as OH, CH, C_2, CN and NH can be detected spectroscopically in the inner cones of organic flames. In some cases, e.g. with OH, the radicals are believed to play an important part in the combustion reactions. Many of these radicals, however, such as CH and C_2, are not usually included in the ordinary combustion mechanism, and the nature of their role in the combustion is highly speculative. Nevertheless the emission of light by these radicals is a very characteristic feature of the spectra of the inner cones of flames of the Bunsen-burner type. In the ordinary Bunsen flame at atmospheric pressure the inner cone consists of a roughly conical zone of highly luminous reacting gases which is very thin, being only of the order 0·1 to 0·01 mm. thick. In a flame of this type spectroscopic examination may show the

presence of certain radicals, but there is no means of determining at what stage in the very rapid reactions taking place in the flame these radicals are formed.

One of us (H. G. W.) has studied some stationary flames of pre-mixed gases burning at relatively very low pressures. In these flames the reaction zone is very much thicker than at atmospheric pressure, and may in some cases exceed a centimetre; also by suitable control of gas flow and pressure, it is possible to obtain flames in the shape of a flat disc instead of a cone. These thick, flat flames are particularly suitable for detailed study. This work is now being continued by us at the Imperial College, London, and it is the purpose of this short paper to report the results of some preliminary spectroscopic observations on these low-pressure flames.

Experimental and Results.

Low-pressure Flames.

In these flames the premixed gases are burnt at a quartz or hard-glass jet in a large glass vessel which is continuously evacuated by a powerful rotary oil-pump. This vessel is fitted with quartz windows for viewing the flame and with electrodes for ignition; in the earlier work molybdenum electrodes sealed through the glass were used, but recently steel electrodes waxed in through protecting Pyrex sleeves have been found satisfactory. A fan served to cool the vessel and prevent the wax on the windows and electrodes from softening. The vessel is evacuated through an adjustable valve which enables the pressure in the vessel to be controlled; a large (200 l.) reservoir between the valve and the pump serves to steady the pressure. It has been found [1] that the lowest pressure at which a flame can be maintained depends on the size of the burner, and varies approximately inversely with the diameter of the burner. Hence to reach very low pressures, of the order of a few mm. Hg, it is necessary to use very large burners, with consequently high gas flows and pumping speeds. Most of the results reported here have been obtained using a burner of about 34 mm. diameter and total gas flows of around 5 cu. ft./hr. (measured at N.T.P.).

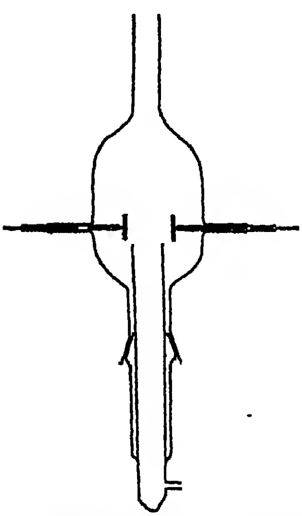

FIG. 1.—Diagram of flame vessel. The quartz windows are omitted for clarity in presentation.

For any given burner diameter and gas mixture there is a critical pressure below which a steady flame cannot be maintained, and at this critical pressure there is a corresponding value of the mass flow of gases at which the flame can just, and only just, be maintained. At pressures above the critical pressure the flame can be held over a range of mass-flows; for too high a gas-flow the gas velocity exceeds the burning velocity and the flame blows off; for too low a mass-flow the flame either strikes back or is extinguished through cooling to the burner walls as it attempts to strike back. For pressures and mass-flows which are well above the critical values, the flame is conical, rather like the inner cone of an ordinary Bunsen flame but more rounded, and if the pressure is raised the flame strikes back while still an irregular shape. For mass-flows a little above the critical value it is possible to adjust the pressure so that a flat flame is obtained. Table I serves to illustrate the approximate pressures, gas-flows, and thicknesses of flame for various stoichiometric gas mixtures for convenient running; these do not represent the absolute minimum pressures at which the flames can be

[1] Wolfhard, *Z. tech. Physik.*, 1943, 9, 206.

this type of flame some condensation products are formed and these cloud the walls of the vessel in time

METHANE —The general appearance of the flame is rather similar to that of acetylene but the C_2 bands are rather less strong the reaction zone is a little less thick and the minimum pressure is higher With a stoichiometric mixture the upper part of the flame is again rather violet with the CH bands strong but the green base to the flame is less noticeable than with acetylene However, photographs of the spectrum again suggest that the C_2 commences a little lower than CH in the flames and also in flames of mixtures of methane and hydrogen the C_2 comes very definitely at a lower level than CH so the differences between the methane and acetylene flames are probably ones of degree rather than kind In weak mixtures CH is again relatively strengthened compared with C_2, and the HCO bands again occur The HCO and OH commence below CH.

With slightly rich mixtures the flame develops a green outer ring, showing C_2 With very rich mixtures the bands of CH occur below those of C_2, this is the reverse position to that of mixtures around the stoichiometric value

BUTANE —This flame is very similar to that of acetylene or methane, with a definite greenish base showing C_2 In very weak mixtures the HCO bands are particularly strong

ETHYLENE —The oxy ethylene flame is again very similar to that of acetylene, and usually shows the C_2 bands commencing definitely below those of CH We have, however, obtained some spectrograms of a very rich mixture, about the richest mixture which will give a steady flame and this shows a pale violet-blue base emitting chiefly CH bands and a bright green main zone emitting C_2, with a weak luminous cap above showing a continuum from hot carbon particles A spectrogram is reproduced in Plate I*b* With very weak mixtures the HCO bands are observed, but we have not obtained them as strongly with ethylene as with acetylene or butane This is a little surprising as these bands were originally obtained by Vaidya in the ethylene flame and known as ethylene flame bands

Flames with Nitrous Oxide.

Some preliminary observations have been made on the low pressure flames of various gases burning with nitrous oxide instead of oxygen These show in addition to the previous radicals CH, C_2 and OH, bands due to the radicals CN, NH and NH_2 The γ-bands of NO also occur In these flames the reaction zone is rather thinner than in the flames with oxygen, but it is still possible in some cases to say which radicals occur early and late during the combustion process

HYDROGEN —In this flame the bands of OH, NH and NO appear in about the same region, but the ammonia α-band, which is usually attributed to the radical NH_2, extends appreciably higher in the flame, as can be seen in Plate I*c*

ACETYLENE —In the acetylene-nitrous oxide flame the C_2 bands occur lowest in the flame, with CH and CN higher up The OH and NH extend through the flame and it is difficult to say whether they commence with, or slightly above, the C_2 The bands of OH NH and NO are much less sharply localised than those of C_2, CH and CN and they extend a good deal higher in the flame In this flame also the NH_2 bands commence at a rather higher level than those of NH

METHANE —The observations on the methane flame are closely similar to those on acetylene

Discussion.

At this preliminary stage of the investigations it is difficult to draw any certain conclusions about either the detailed reactions of the various free radicals or the combustion mechanism but a few speculations may be hazarded The reactions in flames at low pressures, of the order of 1/100th atmosphere cannot be expected to be identical quantitatively with those in flames at atmospheric pressure In particular, low-pressure flames will favour bimolecular reactions at the expense of termolecular or higher order reactions Also in the low-pressure flames there is rather more dissociation and hence a relatively higher concentration of free atoms and radicals such as OH Nevertheless the general appearance, behaviour and spectra of these low-pressure flames are remarkably similar to those of Bunsen-type flames, and it is natural to conclude that the reactions at low pressure are qualitatively, if not quantitatively, very similar

The outstanding observation is that in hydrocarbon flames with weak or roughly stoichiometric mixtures the bands of C_2 precede the CH bands. It would be natural to regard the removal of hydrogen from the hydrocarbon, perhaps by reaction with H atoms or OH radicals, as taking place in successive steps so that CH might precede carbon. Actually the reverse is usually true. A reaction of the type :

$$C_2 + OH = CO + CH,$$

which is very exothermic, might account, on the other hand, for the CH bands appearing at a later stage than C_2. It is probable that the formation of solid carbon and C_2 is due to polymerisation and subsequent cracking of the hydrocarbons (Gaydon and Whittingham [3]) and we may now suppose that the formation of CH in flames is partly due to reaction of C_2 with OH, or perhaps with hydrogen or water. With mixtures which are very rich in fuel, however, the CH bands may occur below the C_2 so that there must presumably be some independent mechanism by which CH can be formed without the prior formation of C_2.

It is interesting that Vaidya's hydrocarbon flame bands occur in the early stages of combustion, before CH. It has been shown (Gaydon [4]) that in some cases the presence of these bands, which are believed to be due to HCO, is associated with the formation of peroxides in the combustion. These peroxides would presumably be formed in the earliest stages of reaction, so that the presence of HCO, formed by decomposition of the peroxides, is to be expected fairly early in the reaction.

The occurrence of NH_2 (ammonia α-band) at a later stage than NH in the flames with nitrous oxide is not surprising. The fact that the bands of the CN radical tend to occur, with CH, rather above the region where C_2 is strongest, suggests that the CN is formed by reaction of carbon with nitrous oxide rather than by direct reaction of the hydrocarbon with N_2O.

These low-pressure flames tend to favour the emission of light by chemiluminescence, because of the longer time between deactivating collisions, and any delays in the equipartition of vibrational or rotational energy are more likely to show up. Some interesting observations on the chemiluminescent excitation of OH radicals in flames and on anomalies in the vibrational intensity distribution in the OH bands are being made and will be reported separately in due course.

Summary.

In flames at very low pressures ($\sim$ 1/100 atm.) the reaction zone, corresponding to the inner cone of a Bunsen-burner flame, is much thicker, and it is possible to study in detail, by spectroscopic methods, the formation of radicals such as OH, CH, C_2, HCO and CN. In hydrocarbon flames the C_2 and OH bands are emitted at an earlier stage of the reaction than CH; Vaidya's hydrocarbon flame bands, which are probably emitted by the radical HCO, also occur early in the reaction. In flames supported by nitrous oxide the radicals C_2 and NH appear to be formed before CN and NH_2. The mechanism of formation of some of the radicals has been briefly discussed.

Résumé.

On a fait l'étude spectroscopique de la formation de radicaux dans des flammes à basse pression (1/100 atm.). Dans des flammes d'hydrocarbures, les bandes de C_2 et de OH sont émises plutôt que celles de CH. Les bandes de flammes d'hydrocarbures, décrites par Vaiyda et probablement émises par HCO, apparaissent de bonne heure dans la réaction. Dans des flammes entretenues par N_2O, les radicaux C_2 et NH apparaissent avant CN et NH_2. Le mécanisme de formation de quelques uns de ces radicaux est brièvement discuté.

[3] Gaydon and Whittingham, *Proc. Roy. Soc. A*, 1947, 189, 313.
[4] Gaydon, *ibid.*, 1942, 179, 439.

Zusammenfassung.

Die Bildung von Radikalen in Flammen bei niedrigen Drucken (1/100 at.) ist spektroskopisch untersucht worden. In Kohlenwasserstoffflammen treten die C_2 und OH Banden früher als die CH Banden auf. Vaidya's Kohlenwasserstoffflammenbanden, die wahrscheinlich von HCO ausgegeben werden, treten auch zeitlich in der Reaktion auf. In von N_2O unterstützten Flammen erscheinen die Radikale C_2 und NH vor CN und NH_2. Der Bildungsmechanismus einiger dieser Radikale wird kurz erörtert.

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THE RADICALS BrO AND CBr IN FLAMES.

By E. H. Coleman and A. G. Gaydon.

Received 22nd July, 1947.

The extensive use of methyl bromide as a fire extinguisher makes it important to know the mechanism of its inhibitory action, and for this purpose a study of its flame spectrum has been made. Vaidya [1] found that a system of bands in the region 4000-4600 A. was obtained in the flame of ethyl bromide burning with oxygen, and he assigned them provisionally to the radical BrO. In flames containing chlorine compounds, however, bands due to CCl, not ClO, are observed, and one of us (Gaydon [2]) suggested that the bands observed by Vaidya might equally well be due to CBr. The emission spectra of flames containing oxygen, hydrogen, methyl bromide, and bromine, have therefore been studied in order to determine the emitter of the bands.

Experimental.

The following flames have been studied.

(*a*) Hydrogen burning in air.
(*b*) Hydrogen with methyl bromide burning in air, and in oxygen.
(*c*) Hydrogen burning in oxygen with bromine.
(*d*) Oxygen burning in atmospheres of hydrogen with, and without, methyl bromide.
(*e*) Premixed oxygen and methyl bromide burning in air.
(*f*) Mixtures of oxygen, hydrogen, and methyl bromide burning in a Smithell's separator so that the inner and outer cones could be studied separately.

The gases were obtained from commercial cylinders, and the bromine was introduced by passing oxygen over liquid bromine. The gases were burned at quartz jets. The spectra were photographed with a small quartz spectrograph of relatively wide aperture and some plates, including those reproduced, were taken with a medium quartz instrument, Zeiss Q24.

Effect of Methyl Bromide and Bromine on Flames.

The first effect of the addition of a little methyl bromide to a flame is the development of an inner cone which increases in size with further additions of bromide; a bronze-coloured fringe to the outer mantle is also formed. As the methyl bromide content is increased, a grey fringe develops round the inner cone, the mantle increases in luminosity, and finally the flame becomes smoky. The oxy-methyl-bromide flame has a blue inner cone surrounded by a lilac-coloured

[1] *Proc. Indian Acad. Sci.*, 1938, *7a*, 321.
[2] *Spectroscopy and Combustion Theory* (Chapman and Hall, 1942), p. 74.

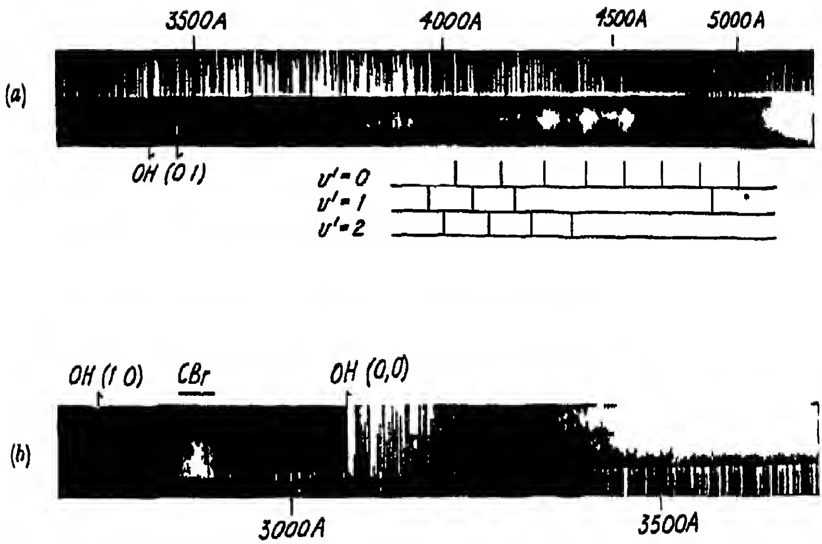

PLATE I

(a) Spectrum of flame of hydrogen in oxygen with bromine medium quartz spectrograph 40 min exposure panchromatic process plate The BrO bands are indicated Fe comparison above

(b) Spectrum of inner cone of oxy methyl bromide flame showing band attributed to CBr Medium quartz spectrograph, 16 min exposure on Zenith plate Fe comparison below

[To face page 167

zone. The outer fringe is light brown. When hydrogen is burned in oxygen to which about 4·5 % bromine vapour (by volume) has been added, a blue inner cone is formed and the outer mantle is brown; the flame is several times larger than the corresponding flame without bromine. The inflammability limits of the oxy-methyl-bromide flame were approximately 19·5 % and 31·0 % methyl bromide.

Spectroscopic Observations.

Oxy-methyl-bromide Flames. The bluish inner cone shows bands chiefly due to OH, CH, and C_2. There is also a hitherto unobserved band round 2900 A. In the lilac zone just above the inner cone, Vaidya's bands (BrO) are strong, as also are bands at the red end due to Br_2. The bronze tip of the flame shows chiefly Br_2 and OH bands. Vaidya's bands extend into this zone but are relatively less strong. The band at 2900 A. occurs best with the weaker mixtures, and, also, in these mixtures the CH is relatively less strong than the C_2. The zones of the flame in which the bands occur are shown in Fig. 1.

Flames of Oxygen in Hydrogen with Methyl Bromide. The flame of oxygen burning in an atmosphere of hydrogen to which methyl bromide has been added shows very strong OH bands with Vaidya's (BrO) bands present weakly, and Br_2 bands in the red region.

Diffusion Flames of Hydrogen with Methyl Bromide Burning in Air and Oxygen. The diffusion flames of hydrogen with methyl bromide show strong CH bands, Vaidya's (BrO) bands, Br_2 bands, and a little CH.

Premixed Oxygen, Hydrogen, and Methyl Bromide Burning in a Smithell's Separator. The flame of the premixed gases oxygen, hydrogen, and methyl bromide, showed C_2, CH, and OH in the inner cone, and the 2900 A. band is present faintly. The zone above the inner cone shows Vaidya's (BrO) bands and OH. The outer cone shows Br_2 and continuum.

Hydrogen Burning in an Atmosphere of Oxygen and Bromine. The blue inner cone of the flame of hydrogen burning in an atmosphere of oxygen and bromine shows Vaidya's (BrO) bands quite strongly. This indicates that the bands are due to BrO rather than to CBr since no carbon is present in the flame.

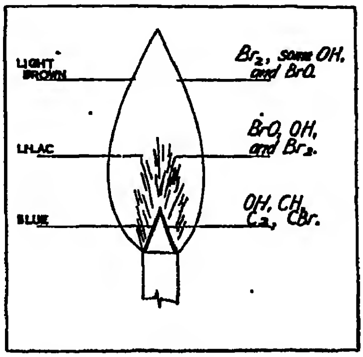

Fig. 1.

The Spectrum of BrO.

We have seen that Vaidya's ethyl bromide flame bands are most probably due to BrO, since they occur when pure bromine is added to the oxygen atmosphere in which hydrogen is burning. Vaidya measured the heads of 8 bands and gave a provisional vibration scheme. In our plates (Plate 1*a*) we have observed additional bands; and since C_2 and CH are not present we have been able to measure bands which were masked on Vaidya's plates. The bands are degraded to the red, but the heads are diffuse and it is far from easy to make precise measurements. We have, however, obtained rough estimates to the nearest A. of the heads of 16 of these bands and these are presented in Table I. Our spectra were taken on a medium quartz spectrograph which would justify measurements to better than 0·1 A., but the diffuseness of the bands precludes this.

There is one obvious strong progression of bands, presumably the $v' = 0$ progression, and the remaining bands can be arranged into two other progressions to give the scheme set out in Table II. This is essentially an extension of Vaidya's scheme, but the wavelength of the (1, 2) band has been changed from 4178 to 4186 A. permitting the inclusion of one band which he gave as 4065·8 A. and could not include in his scheme. His

band at 4430 A. was not observed. The assignment of the values of v'' is provisional; it is possible that they may require raising by one or more units, but the vibrational and intensity distribution favours the present assignment.

In addition to the main BrO bands listed we, like Vaidya, observed other bands of shorter wavelength in the ultra-violet, but owing to their faintness and overlapping by OH it was not possible to attempt measurement and analysis. The strongest two heads appear to be at 3333 and 3384 A.

TABLE I.—BAND HEADS OF BrO.

λ.	Int.	ν.	v', v''.	λ.	Int.	ν.	v', v''.
4965	1	20135	0, 7	4225	2	23662	2, 3
4856	2	20587	1, 7	4186	3	23882	1, 2
4817	3	20754	0, 6	4147	6	24107	0, 1
4673	8	21394	0, 5	4109	4.	24330	2, 2
4533	10	22055	0, 4	4069	5	24569	1, 1
4398	10	22731	0, 3	4029	3	24813	0, 0
4349	4	22987	2, 4	3999	3	24999	2, 1
4270	10	23413	0, 2	3958	3	25258	1, 0

By using the bands of the main $v' = 0$ progression we can give approximate values for the vibrational constants of the ground state. ω_e comes about 713 cm.$^{-1}$ and $x_e\omega_e = 7$ cm.$^{-1}$. A linear Birge-Sponer extrapolation gives 17800 cm.$^{-1}$ or 2·2 E.V. for the dissociation energy of the ground state of BrO. As is well known (cp. Gaydon[8]) the linear extrapolation usually comes too high by perhaps 20 %, and the more probable value for the heat of dissociation is 1·75 E.V. $\pm$ 0·3 or 40 kcal. This compares with an estimated value of 44 kcal. for the dissociation energy of ClO. Taking this value of 40 kcal. for the dissociation energy of BrO, the heat of formation of BrO from bromine and oxygen in their standard states would be about $-$ 46 kcal.

TABLE II.—VIBRATIONAL SCHEME FOR BrO.

v', v''.	0.		1.		2.		3.		4.		5.		6.		7.
0	24813		24107		23413		22731		22055		21394		20754		20135
	445	706	462	694	469	682		676		661		640		619	452
1	25258		24569		23882										20587
		689	430	687	448										
2			24999		24330		23662		22987						
				669		668		675							

It may be noted that the BrO bands occur above, not in, the inner cone. A possible reaction for the formation of BrO is:

$$Br_2 + OH = HBr + BrO$$

which would be slightly endothermic. It is improbable that the BrO is formed in the initial oxidation of methyl bromide.

The Band at 2900 A.

As already mentioned, a diffuse band has been observed about 2900 A. It is shown in Plate 1*b*. The band appears to be diffuse without obvious heads, and is rather badly masked by the overlapping (1, 0) OH band.

[8] *Dissociation Energies* (Chapman and Hall, 1947).

Bands due to CCl have been observed by Asundi and Karim,[4] the (0, 0) sequence is at 2796 A. and the bands have a rather complex structure. Vaidya [5] has observed them in flames of, or containing, methyl chloride, chloroform, and carbon tetrachloride. The new band at 2900 A. occurs in the inner cone of the flames in much the same zone, and in similar conditions as CH. It only occurs with methyl bromide and not in the hydrogen flame in oxygen with bromine. The similarity of region between this band at 2900 A. and the CCl band at about 2800 A., and the conditions of its occurrence suggest strongly that the new band is due to CBr.*

This work is part of an investigation being made by the Fire Research Organisation into the mechanism of fire extinction, and is published by permission of the Director, Fire Research Organisation, Department of Scientific and Industrial Research.

The authors wish to thank Dr. W. M. Vaidya for helpful criticism, and one of us, A. G. G., is indebted to the Royal Society for the award of a Warren Research Fellowship.

Summary.

The spectra of flames containing methyl bromide and of flames containing bromine vapour have been examined. Bands in the region 3800-5000 A. previously observed by Vaidya in an ethyl bromide flame have been obtained in a flame of hydrogen burning in oxygen and bromine; this supports Vaidya's assignment to BrO rather than to CBr. Further measurements, and an extended vibrational analysis of these bands are presented; a provisional value for the heat of formation of BrO is given. In flames containing methyl bromide, a diffuse band is observed in the region 2900 A.; this is provisionally attributed to CBr.

Résumé.

Les spectres de flamme, contenant (1) CH_3Br et (2) Br_2 gazeux ont été examinés. Des bandes dans la région 3800-5000 A. pour la flamme de H_2 brûlant dans O_2 et Br_2, viennent appuyer l'attribution de ces bandes par Vaiyda à BrO plutôt qu'à CBr. On donne d'autres mesures, ainsi qu'une analyse des vibrations des bandes et une valeur provisoire pour la chaleur de formation de BrO. Une bande diffuse à 2900 A. pour des flammes contenant CH_3Br est actuellement attribuée à CBr.

Zusammenfassung.

Die Spektren von Flammen, die (*a*) CH_3Br und (*b*) Br_2-Dampf enthalten, wurden untersucht. Banden im Gebiet 3800-5000 A., die in der Flamme von in O_2 und Br_2 brennendem H_2 gefunden werden, unterstützen deren Zuordnung (von Vaidya) zu BrO und nicht zu CBr. Weitere Messungen und Kernschwingungsfrequenzanalyse der Banden, sowie ein provisorischer Wert für die Bildungswärme von BrO werden angegeben. Ein diffuses Band bei 2900 A. in Flammen, die CH_3Br enthalten, wird vorläufig CBr zugeschrieben.

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[4] *Proc. Indian Acad. Sci.*, 1937, *6a*, 328.
[5] *Proc. Roy. Soc. A.*, 1941, 178, 356.
* Note added in Proof: Later work favours Br_2 (see Discussion, p. 176).

GENERAL DISCUSSION

Dr. G. J. Minkoff (*London*) said: I should like to mention two papers recently published, which have a direct bearing on my paper. I have referred to the apparent inconsistency in the mechanism of the photochemical union of hydrogen and oxygen, which suggests that the reaction, $H_2 + HO_2 \rightarrow H_2O_2 + H$, proceeds at every collision at room temperature, even though it is known not to occur frequently at moderately high temperatures. The postulation of the reaction was made partly to account for the yield of 88 % H_2O_2, and partly to account for quantum yields greater than unity which were found by earlier workers. Volman,[1] a co-worker of Rodebush, has now investigated the reaction with the aid of a more reliable actinometer, and he has found that a more correct value for the quantum yield is 0·3-0·6 % mol. H_2O_2 per quantum of light absorbed. There is thus no longer any need for H_2O_2 to be formed together with a chain carrier under these conditions. Volman suggests that reactions[2] such as $2\,HO_2 \rightarrow H_2O_2 + O_2$ may be of importance. In this way, the photochemical reaction falls into line with the thermal reaction.

The other paper describes the mass-spectrographic technique developed by Eltenton[3] for studying combustion processes. It was found that when a low-pressure methane- or propane- oxygen mixture was ignited, the current due to ions of mass 33 increased simultaneously with a decrease in the current due to mass 32 ($O^{16}O^{16}$). This is strong evidence for the presence of the radical HO_2 in flames.

Dr. F. S. Dainton (*Cambridge*) (*communicated*): I would like to raise one point in connection with Dr. Minkoff's paper. All previous workers on the hydrogen-oxygen reaction are agreed that in the three-body reaction,

$$H + O_2 + M \rightarrow HO_2 + M^*,$$

hydrogen is as efficient a third body as its mass and collision diameter would lead one to expect. To account for Dr. Minkoff's data on hydrogen peroxide formation, the HO_2^* radical when formed by the binary process, $H + O_2 \rightarrow HO_2^*$ (retaining the energy of formation), must be presumed capable of reaction with hydrogen according to $HO_2^* + H_2 \rightarrow H_2O_2 + H$ at nearly every collision. Does the theoretical treatment indicate why the assembly of $H + O_2 + H_2$ under the same conditions of energy can yield such dissimilar results in the ternary, and double binary processes?

Dr. G. J. Minkoff (*London*) (*communicated*): It would be expected that the double binary process, $H + O_2 \rightarrow HO_2^*$, $HO_2^* + H_2 \rightarrow H_2O_2 + H$, would be more efficient in producing H_2O_2 than a direct termolecular collision of $H + O_2 + H_2$, other factors being equal, because the steric factor is less important in the former process. It is clearly more probable that HO_2^* and H_2 will collide in a configuration favourable to reaction than that the three entities, H, H_2 and O_2, will be suitably placed at the time of collision. There is a further factor which explains the higher yield of H_2O_2 by the former process. It is well known that the deactivation of vibrationally-excited molecules by collision with other molecules is relatively inefficient. Studies of the velocity of sound in CO_2 have shown,[4] for example, that the probability of a vibrationally-excited CO_2 molecule will be deactivated on collision with a molecule of CO_2 is 1 in 51,000, 1 in 1,200 for collisions with N_2, and 1 in 60 for collisions with H_2O molecules. Thus, although HO_2^* may be somewhat easier to deactivate than CO_2, there is strong reason to suppose that it will retain its energy of formation until it can react with a H_2 molecule and so give

[1] Volman, *J. Chem. Physics*, 1946, 14, 707.
[2] See Smith and Napravnik, *loc. cit.*
[3] Eltenton, *J. Chem. Physics*, 1947, 15, 454.
[4] Gaydon, *Spectroscopy and Combustion Theory* (London, 1942), p. 110.

H_2O_2. That is to say, a high proportion of the HO_2^* formed by this process will lead to the formation of H_2O_2 and so to a higher yield of H_2O_2 than will the termolecular process, which will produce practically no H_2O_2 when the third body is O_2, H_2O, or H_2O_2, and only a small proportion when the third body is H_2.

Dr. J. Weiss (*Newcastle*) said: Dr. Minkoff has referred in his paper to some calculations regarding the energy of the O_2—H bond energy, which were initiated by Prof. Haber.[5] These calculations should be regarded only as a first approximation as they are made under the assumption that the O atom is in a 3*s* ground state and that the oxygen-oxygen bond is a pure spin valence. It is of some interest, however, that the values which one obtains, applying Heitler's theory, are not greatly dependent on the amount of Coulombic energy which is introduced. This is illustrated by the following figures:

f Q_1 and Q_2 are defined by

$$O_2 + H = HO_2 + Q_1 \text{ kcal.}$$
$$HO_2 + H = H_2O_2 + Q_2 \text{ kcal.}$$

one obtains:

Coulombic Energy.	Q_1 (kcal.).	Q_2 (kcal.).
33%	53	101
20%	48	94

Dr. A. D. Walsh (*Cambridge*) said: Dyne and Style give the first strong evidence in favour of HCO as the emitter of the hydrocarbon flame bands. If we accept this conclusion, it is of importance not only for the theory of reactions in flames but also for the theory of molecular structure. Gaydon[6] has shown that the rotational fine structure of the bands is not sufficiently "open" to permit the emitter having a small moment of inertia such as would be possessed by a molecule HXX with H lying considerably off the XX line. It seems therefore that HCO must be linear, or nearly so.

This is in accord with what would be expected from the ideas stressed in my own paper.[7] The C atom will adopt the condition of hybridisation that leads to the greatest evolution of energy. Both C=O and C—H bonds are likely to have their greatest bond energy (E) when the C atom is close to the acetylenic state, i.e. is forming two hybrid valencies in line.

The conclusion has important consequences. When HCO is formed from HCHO, it is clear that there must be evolved an "energy of reorganisation," since the C valencies change. Comparison of E(CH) in HCHO and C_2H_2 and of E(C=O) in HCHO and CO_2[8] (allowing for certain differences of polarity and other factors in these pairs), makes it difficult to resist the conclusion that the reorganisation energy must be as great as 20 kcal., or more. This reorganisation energy is reflected in the known considerable stability of the HCO radical.[9] Also it implies a marked difference between the dissociation (D) and bond energy for CH in HCHO.

Relative to C_2H_4, the O atom in HCHO is expected to increase the *s* character in the C valency towards H. The effect of this on the CH bond is twofold: it should strengthen it by increase of the bond electronegativity product but at the same time weaken it by increase of the bond electronegativity difference (or polarity). The resultant of these should be a strengthening as in C_2H_2; but the matter is complicated by interaction of the electrons occupying the O 2*p* lone-pair orbital (whose spatial spread is likely to be considerable since its ionisation potential

[5] Cf. Weiss, *Trans. Faraday Soc.*, 1935, **31**, 668.
[6] Gaydon, *Spectroscopy and Combustion Theory* (Chapman and Hall, 1942), p. 44.
[7] Walsh, this Discussion, p. 18.
[8] See Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60.
[9] Burton, *J. Amer. Chem. Soc.*, 1938, **60**, 212; cf. Style and Summers, *Trans. Faraday Soc.*, 1946, **42**, 388, who find the minimum activation energy for the dissociation of HCO to be 16 kcal.

is only 10·8 v.) and whose axis is in the plane of the CH bonds) with the CH electrons. The electron diffraction value for the CH length (1·09 ± 0·01 A.)[10] suggests a CH bond energy probably within *ca.* 5 kcal. of the CH_4 value (104). The force constant data[11] suggest a rather greater length but the same interaction effects that complicate the theoretical discussion also complicate the interpretation of the force constant as affording a true indication of the bond length. The difficulty with the theory, with the application of the force constant calculations and with the very concept of bond energy is that HCHO is only crudely divisible into two CH bonds and one C=O bond. Remembering this, it is probably wise to take no more than a "blurred" value of the HCHO CH—bond energy as, say 95-110 kcal. A fairly definite conclusion does, however, emerge—namely that, if D *is* 20 kcal., or more, less than E, $D(C—H)_{HCHO}$ is likely to be abnormally low. This conclusion receives support from the ready reaction of atomic H with HCHO in contrast to CH_4;[12] and it is of interest to note that Gorin[13] has placed D(C—H) at 78 kcal. Gorin's estimate implies a value 26 kcal. for $D(C—H)_{HCO}$.

In the ClCO radical (which probably occurs in the photochemical production of $COCl_2$ from CO + Cl_2), there enters the additional factor (relative to HCO) of interaction between the Cl "lone-pair" orbitals and those of the C and O. According to the usual molecular-orbital theory (resulting in the "16 electron" rule), this radical will have a bent configuration.

Dr. K. Wieland (*Zürich*) said: It is well known that at fairly high temperatures, in the region of 1500° c. and higher, quite a large number of diatomic radicals can easily be detected by their absorption spectra.[14] But these spectra if taken under unknown conditions of pressure do not provide any quantitative data concerning the concentrations present. However, I should like to point to the important fact that many absorption spectra of diatomic radicals can be obtained at temperatures below 1200° c. This is important because up to 1200° c. silica tubes can be used as absorption cells and, therefore, the concentration of a radical in thermal equilibrium can be studied under well-defined conditions of pressure and temperature. From the few absorption measurements made under such conditions one may draw the conclusion that very small quantities of radicals can be detected by their absorption spectra. This is illustrated by the above table containing approximate minimum concentrations (in g. mol./l.) which are necessary for the observation of the

Radical.	$C_{min.}$ (g.mol./l).	λ (A).	Reference.
OH	6×10^{-8}	3100	(15)
CN	$\sim 6 \times 10^{-10}$	3880	(16)
CdI	$< 3 \times 10^{-6}$	3400	(17)
HgI	3×10^{-7}	3050	(18)
Molecule.			
O_2	3×10^{-6}	2600	(19)
I_2	3×10^{-6}	5000	(19)
C_6H_6	1×10^{-4}	2550	(19)

[10] Stevenson, Lu Valle and Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 2508.
[11] Linnett, *Trans. Faraday Soc.*, 1945, **41**, 223.
[12] See Long and Norrish, *Proc. Roy. Soc. A*, 1946, **187**, 351. The discussion given here differs in certain respects from that given by these authors.
[13] Gorin, *J. Chem. Physics*, 1939, **7**, 256.
[14] Pearse and Gaydon, *Identification of Molecular Spectra* (Chapman and Hall, London), 1941.
[15] Dwyer and Oldenberg, *J. Chem. Physics*, 1944, **12**, 351.
[16] White, *ibid.*, 1940, **8**, 79 and 459.
[17] Wieland and Herczog, *Helv. Chim. Acta*, 1946, **29**, 1702.
[18] Wieland, *J. Chim. Physique* (in press).
[19] Bonhoeffer and Harteck, *Grundlagen der Photochemie* (Dresden and Leipzig, 1933).

absorption spectra of these radicals in an absorption cell of 10 cm. length. For comparison similar minimum concentrations are also given for some molecules with known absorption coefficients.

The sensitivity of the absorption method depends of course on the spectrograph used. Thus the minimum concentrations obtained for HgI and CdI by Herczog and myself when using only a medium size spectrograph may still be markedly decreased by means of a large grating spectrograph as used by Dwyer and Oldenberg for OH and by White for CN.

Mr. J. R. Arthur and Mr. E. Sterling (*London*) (*communicated*): Examination of the emission spectra of flames discloses the presence of many species of radicals. Considering the violence of the conditions in flames, this is not surprising. As Gaydon has emphasised it cannot be assumed in the absence of other evidence that radicals so detected play a significant part in the main reaction mechanism.

In carbon monoxide flames, however, it is generally recognised that the important labile molecules necessary for flame propagation are derived from moisture or other substances containing hydrogen. In CO flames, it seems certain that both molecular and atomic hydrogen concentrations will quickly reach stationary concentrations. The stability of the flame will only be possible provided those concentrations are greater than a certain minimum value. Moreover, Tanford and Pease[20] have recently made estimates of the H atom concentrations in CO flames and found a definite correlation between burning velocity and these concentrations.

We have recently made some measurements of a stationary hydrogen concentration obtaining during the combustion of carbon monoxide-air mixtures at a jet flame by inserting an evacuated palladium tube in the flame and observing the equilibrium pressure (due to hydrogen) set up within it.[21] The gases fed to the flame were dried over magnesium perchlorate. With the palladium tube at 700° C. (i.e. several hundreds of degrees lower than the flame temperature on account of heat losses by conduction and radiation), we found that:

(i) a steady pressure was quickly reached (Fig. 1*a*);
(ii) there was a rapid response in the pressure to the addition of moisture to the gases fed to the flame (Fig. 1*b*);
(iii) addition and subsequent removal of water from the gases left the hydrogen pressure unchanged so that the diffusion process can be regarded as quantitatively reversible and specific for hydrogen (Fig. 1*c*).

The equilibrium pressure so measured is presumably a property of the flame alone. The rate of approach to equilibrium is a function also of the palladium tube dimensions, and of the volume of the evacuated space. Although the well-known effect of palladium in establishing the equilibrium $H_2 \rightleftharpoons 2H$ precludes the possibility of differentiating between H_2 and H, it is quite clear that the technique represents a method of following the changes in concentration of a labile transient intermediate in the combustion process considered. This would follow of course from the over-simplified reaction scheme suggested many years ago by Dixon:[22]

$$CO + H_2O_2 \rightarrow CO_2 + H_2$$
$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O.$$

It was also found that known inhibitors of the combustion of CO brought about marked decreases in the measured pressure. Fig. 1(*b*) and 1(*c*) show the influence of very small quantities of PCl_3 and HCl on the measured pressure. Indeed, it was found quite generally that those

[20] Tanford and Pease, *J. Chem. Physics*, 1947, 15, 431
[21] Arthur and Sterling, *Nature*, 1947, 160, 869.
[22] Dixon, *J. Chem. Soc.*, 1886, 49, 94.

compounds which markedly increase the CO/CO_2 ratio in the combustion of carbon [23] at 750-850° c. drastically reduce the hydrogen content of a

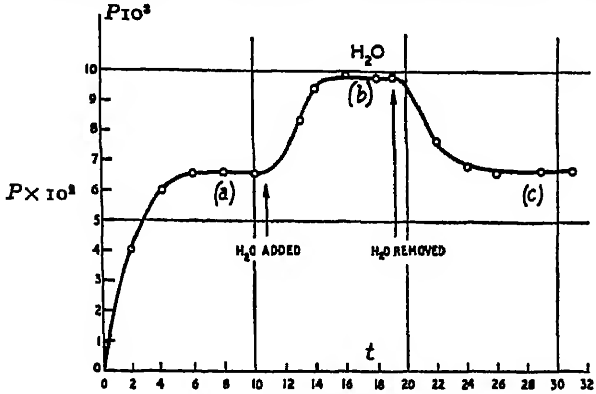

FIG 1(*a*).

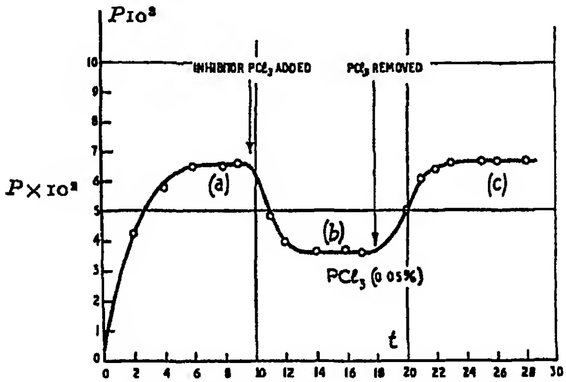

FIG. 1(*b*).

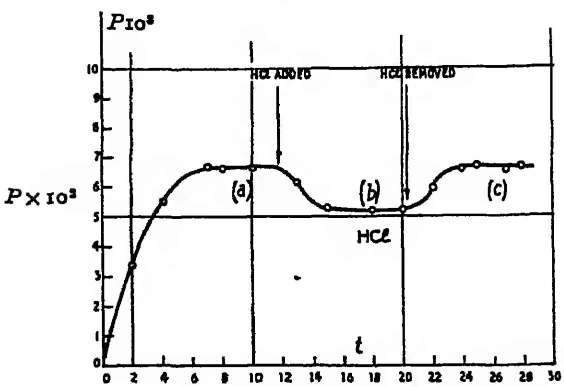

FIG. 1(*c*).

P is partial pressure of hydrogen in mm. Hg.
t is the time in minutes after isolating Pd tube from the evacuating system.

[23] Arthur, *Nature*, 1946, 157, 732. Arthur, Bangham and Thring, *J. Soc. Chem. Ind.* (in press).

CO flame. The technique is likely to be of value in examining the effect of fine solids on reaction rates in flames.

We regard these facts to be of the greatest significance in the fire extinction properties of halogen-containing compounds—a field briefly mentioned by Gaydon and Coleman. Whilst the physical properties such as density are clearly of significance in providing a shielding effect against oxygen, it seems most likely that there is operative a specific retarding influence on the combustion, as Dufraisse and his collaborators [24] suggested some years ago. Since it has been shown [23, 25] that a gas-phase reaction between CO and O_2 certainly plays an important part during the combustion of solid fuels, we ascribe a major part of the fire extinguishing properties of halogen-containing compounds to an inhibitor of the combustion of CO by some such species as elementary chlorine which can combine with chain links. That so many fire-extinguishing agents contain halogen is significant not only on account of the shielding effect arising from high density but also because their electronegative pyrolytic products (chlorine atoms and molecules) suppress the concentration of chain links such as H and H_2.

Dr. G. Whittingham (*Leatherhead*) (*communicated*) : The appearance of electronically-excited CBr radicals in flames containing methyl bromide and the production of a smoky flame when relatively large concentrations of CH_3Br are used suggests that the pyrolysis and combustion of CH_3Br play a large part in determining its role as a fire extinction agent. Owing to the complexity of side reactions likely to take place the pyrolysis of CH_3Br has not received much attention but Meissner and Schumacher [26] found that the principal decomposition products were CH_4, HBr and carbon. They considered that the primary dissociation was

$$CH_3Br = CH_2 + HBr,$$

the methylene radicals then disproportionating to CH_4 and carbon :

$$CH_2 + CH_2 = C + CH_4.$$

The introduction of a bromine atom into the methane molecule brings about marked changes in the reactivity to oxygen.[27] Whereas $CH_4 - O_2$ mixtures, at temperatures of the order of 500-600° c., undergo reaction after long induction periods, similar $CH_3Br—O_2$ mixtures attain explosive velocities after a very short induction period. Moreover the peninsula of inflammation, extending to low temperatures, observed in the ignition of certain $CH_4—O_2$ mixtures is absent with $CH_3Br—O_2$ mixtures of corresponding composition. The presence of this peninsula is usually attributed to the combustion of CO and H_2, products of the primary combustion of CH_4, and its absence in the ignition of $CH_3Br—O_2$ mixtures is considered to be due to the destruction of H atoms or OH radicals by HBr and Br_2 produced in the primary combustion of CH_3Br. As Dr. Gaydon and Mr. Coleman suggest, one product of these chain-breaking processes could be BrO radicals.

Whilst it is evident that chains develop at a high speed in the combustion of CH_3Br it is not easy to see how excited CBr radicals could arise from the reactions of such species as O atoms or OH radicals with CH_3Br molecules. The stripping of H atoms successively from CH_3Br by OH radicals would eventually produce CBr but the reaction

$$CHBr + OH = CBr + H_2O$$

is almost thermo-neutral. It would be interesting to see whether the

[24] Dufraisse and Horclois, *Compt. rend.*, 1931, 192, 564.
[25] Bangham, *Trans. Faraday Soc.*, 1946, 42, 376.
[26] Meissner and Schumacher, *Z. physik. Chem.*, 1940, 185, 435.
[27] Whittingham, *Thesis* (Cambridge, 1942).

intensity of the CH bands in methane flames is influenced by the addition of HBr or Br_2 as the reactions

$$CH + Br_2 = CBr + HBr$$
$$CH + HBr = CBr + H_2$$

are exothermic to the extent of 25 kcal. and 7 kcal. respectively.

Dr. E. H. Coleman and Dr. A. G. Gaydon (*London*) (*communicated*): Dr. Whittingham points out the thermal neutrality of the reaction yielding CBr. Our provisional assignment of the emitter to CBr is not supported by further work which shows that the bands are due to Br_2. With methyl iodide and chloride we have obtained the corresponding bands of I_2 at 3425 A. and Cl_2 at 2580 A. Dr. Wieland stresses the importance of absorption spectra. For following combustion processes, however, there are two difficulties; firstly, the small concentrations and short path lengths, and secondly, the radicals excited by chemiluminescence have such a high effective temperature that it is difficult to obtain a sufficiently hot background source to give reversal.

III.—THE LIQUID PHASE.

INTRODUCTORY SURVEY.

By W. A. Waters.

Received 12th September, 1947.

Only ten years have elapsed since the possibility that free radicals might be concerned in a few, somewhat abnormal, reactions in solution was first reviewed,[1] and in this period knowledge of homolytic reactions in solution has advanced at an astonishing rate. The greatest development of the subject lies in the field of polymerisation chemistry, which is being accorded specialised treatment at this meeting, but it is worth while to recall now that the present quantitative development of this technically important subject has depended upon the outcome of those exploratory studies of the reactions of dibenzoyl peroxide which indicated that it yielded free neutral phenyl radicals in solution, and which showed that these active radicals then initiated reaction-chains which, with olefines involved radical addition to one end of a double bond, and with saturated molecules involved atom transfer whereby one free radical was converted into another. The respective roles of solvent and solute molecules then became clear, and it was seen that the circumstances under which dissolved substances might act as retarders, or inhibitors, of the reaction-chain depended essentially upon the intrinsic energy contents of the free radicals which they might generate.[2]

To-day the study of polymerisation chemistry has developed so rapidly that it has become the main source of exact information concerning the degree of reactivity of any specific free radical in solution. It is to be hoped, therefore, that the intense specialisation which is occurring in this field will not be such as to obscure the general applicability of its quantitative conclusions concerning free-radical kinetics. Many other important reactions, as for instance oxidation processes, can be explained by the use of the same fundamental theories, and their development will largely depend upon the extent to which their quantitative aspects can be elucidated. Already papers presented at this meeting are indicating how this can be done. The contribution of Dr. Bolland and Dr. ten Have (p. 252)

[1] Hey and Waters, *Chem. Rev.*, 1937, **21**, 186.
[2] Waters, *Trans. Faraday Soc.*, 1941, **37**, 770.

gives us a very striking instance of the way in which an exact kinetic study can identify as R—O—O• the essential free radical concerned in what is after all a very complicated reaction process, whilst the paper by Miss Stead and Dr. Denbigh (p. 263) deserves consideration in that it may give us a helpful new technique for investigating labile molecules of interest.

New methods of producing free radicals in solution should always receive particular attention, since they constitute the starting-points of new avenues of research. Photolytic processes in solution, such as those described by Mr. Olearts and Prof. Jungers (p. 222) have as yet received far too little study, whilst the decompositions of very unstable organometallic compounds which are described by Dr. Bawn and Mr. Whitby (p. 228), offer almost unlimited scope to the organic chemist. Coming from quite another angle, Dr. Mann's paper (p. 236) gives us a reminder that there can be many types of electron-deficient labile molecules besides the analogues of free methyl or free phenyl with which we are now fairly well acquainted.

We are still in the exploratory stage of free-radical chemistry, in which certain reactions, as, for instance, the Cannizzaro reaction are for a time thought to be free-radical processes,[3] and then turn out to be substantially otherwise [4] whilst others, somewhat unexpectedly, do seem to have some free-radical character. It is as exploratory studies that we should view the contributions of Prof. Fieser (p. 242) and of Dr. Birch (p. 246), which deal with oxidation and reduction processes respectively. Both these papers give valuable indications as to what are the critical centres at which complex molecules can be attacked by electron-abstracting and electron-supplying reagents, and though the observable reaction-product is rarely of free-radical character there is still a good reason to believe that the initial change may be a one-electron process.

Only two years ago the Faraday Society, at a meeting in London, heard an interesting exploratory paper which dealt with a process of "reduction-activation" [5] whereby peroxides and persulphates could become polymerisation catalysts. One of these recuction-activations was then shown by Baxendale, Evans and Park [6] to be a *one-electron* transfer process in which a ferrous ion disrupted the weak O—O link of hydrogen peroxide, and set free the intensely reactive free radical hydroxyl, •OH.

Several years before this Haber and Weiss [7] had postulated the same electron-transfer reaction, viz.,

$$Fe^{++} + HO{-}OH \longrightarrow Fe^{+++} + (HO:)^{-} + {}^{\bullet}OH$$

as one of the chain-starting processes involved in the catalase type of decomposition of hydrogen peroxide to oxygen and water, and in a series of speculative papers Weiss had developed the view that peroxidase oxidations also involve this radical, but not until Evans and his colleagues showed that free hydroxyl was a typical polymerisation catalyst, which became incorporated into the end groups of the resulting polymerised products [8] were these views firmly substantiated in such a way that the Haber-Weiss conception could be developed quantitatively. To-day we can see quite clearly the great significance of one-electron transfer processes.

Dr. George (p. 196) has shown that the original Haber-Weiss scheme for the catalase decomposition of hydrogen peroxide is not quite correct by studying the particular properties of the $HO_2^{\bullet}$ radical, which can be

[3] Cf. Weiss, *Trans. Faraday Soc.*, 1941, **37**, 782.
[4] Alexander, *J. Amer. Chem. Soc.*, 1947, **69**, 289.
[5] Bacon, *Trans. Faraday Soc.*, 1946, **42**, 140.
[6] *Ibid.*, 1946, **42**, 155.
[7] Haber and Weiss, *Proc. Roy. Soc., A.* 1934, **147**, 332.
[8] Evans, *J. Chem. Soc.*, 1947, 266.

obtained from that curious substance, potassium peroxide, KO_2, and his work will interest all those who are concerned with the decompositions of organic peroxides.

Dr. Weiss (p. 188) and the writer (p. 179) have concerned themselves with specific reactions of the free hydroxyl radical, and in consequence have established the occurrence, in aqueous solution, of a whole series of new free radicals, such as $\cdot OOC—COOH$ from oxalic acid, $R'\dot{C}H—OH$ and $R''\dot{C}—OH$ from alcohols, and $R—\dot{C}{=}O$ from aldehydes; the last of these had previously been encountered (though not hydrated) as a transient photochemical decomposition product of aldehyde and ketone vapours. In addition to demonstrating the free-radical nature of oxidations involving peroxides, the quantitative aspects of these papers are valuable, for they indicate how the rates of the various reactions of free hydroxyl, such as addition to C=C or abstraction of hydrogen from H—C, can all be compared by reference to one standard reaction, i.e. the electron transfer:

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + (:OH)^-.$$

Thus, in the past two years quantitative chemistry has made another big stride forward towards the interpretation of what has hitherto been one of the most puzzling of all groups of catalysed reactions; i.e. oxidase systems. So many metallic, and other ions, can undergo one-electron oxidation or reduction, that it may not be too rash a prediction to suggest that here, in this meeting's papers, we shall find the underlying theoretical explanations of the actions of most of those trace elements which are so important in biochemistry, and so vitally significant in relation to both medicine and agriculture.

Still another feature of these papers on free-radical reactions in aqueous solution deserves special comment. The free hydroxyl radical is particularly important in water, because any more active radical which we may manage to generate in water would immediately be converted to free hydroxyl by chain transfer of the type:

$$R\cdot + H—OH \longrightarrow R—H + \cdot OH$$

(compare, $Cl\cdot$ (*atomic*) $+ H—OH \longrightarrow HCl + \cdot OH$)

whereupon hydroxyl will have an *apparently* long existence on account of solvent exchange:

$$HO\cdot + H—OH \rightleftharpoons \mathit{HO}—H + \cdot OH.$$

If, however, our aqueous solution contains a solute molecule, R—O—H (e.g. an alcohol) or an anion X^- (e.g. I^-) which by hydrogen, or electron abstraction gives a less reactive free radical than hydroxyl then a similar chain transfer will occur,[9] e.g.

$$HO\cdot + I^- \longrightarrow (HO:) + I^\circ.$$

Employing the terminology of investigators of polymerisation, we would describe these molecules, or ions, as retarders, or, if they are sufficiently distinct, as inhibitors of our oxidase systems. Effects of inhibiting or poisoning agents are recorded in abundance in the vast literature of enzyme chemistry, and it may well be that we shall soon be able to explain them, and perhaps also be able to account for much of the specificity of enzyme oxidations, in the light of our studies of chain transfer.[10] Polymerisation research is showing us that even a small change of an activation energy, or of a reaction velocity constant, can vastly change the nature of the final product in a system in which there are only two competing chain reactants (e.g. two monomeric olefines in a co-polymerisation process), and that in consequence careful quantitative work is needed before competitive chain reactions can really be understood. In future it will therefore be essential to pay an equally careful attention to the quantitative aspects of electron-transfer chemistry.

[9] Cf. ref. 2. [10] Cf. Waters, *Trans. Faraday Soc.*, 1943, 39, 142.

Our theoretical information as to the energy contents of free radicals is undoubtedly of great value, but it is only by measuring reaction velocities, and activation energies, for free-radical processes in solution that we can hope to answer the vital question as to how much the reactivity of a free radical is a function of its environment. It has been suggested [8] that the electrical neutrality of a radical makes its reactivity far less dependent upon the polar nature of the solvent which surrounds it than is the case with a reacting ion, but though it may be reasonably justifiable to neglect the environmental influence of free radicals in non-polar solvents, such as hydrocarbons, this simplification is certainly inadmissible for reactions in polar solvents such as water, which may even solvate our labile molecules. For these reasons we must beware of letting speculations run far ahead of experimental research in this most promising, new field of chemistry. The following papers, however, present so much that is novel that it may not be long before we find that its subject matter forms the basis of an entire future meeting of the Faraday Society.

Dyson Perrins Laboratories,
Oxford.

A.—ELECTRON-TRANSFER REACTIONS.

THE MECHANISM OF OXIDATION OF ALCOHOLS WITH FENTON'S REAGENT.

By J. H. Merz and William A. Waters.

Received 3rd July, 1947.

One of us [1] has already pointed out that chain-reaction schemes involving free hydroxyl radicals can provide satisfactory qualitative explanations of Fenton's reactions [2] whereby polyhydric alcohols, α-hydroxy acids and carbohydrates have been oxidised rapidly by cold hydrogen peroxide in the presence of a ferrous salt. This reaction has hitherto received but little quantitative study. The numerous experiments of Wieland and his colleagues [3] are unfortunately of but little value to-day, since these workers used a large excess of hydrogen peroxide, which appreciably attacked the products of the initial iron-catalysed oxidation. Of more value is the work of Goldschmidt and Pauncz [4] who showed that (contrary to the statements of Fenton [2a] who used an excess of hydrogen peroxide and therefore failed to detect aldehyde) even the simple monohydric alcohols are rapidly oxidised by cold hydrogen peroxide in the presence of any ferrous salt. They showed that the reaction was not due to peroxides of iron, and considered that the process was a chain reaction involving the *same* reactive intermediate as that which is concerned in the "catalase" decomposition : $2H_2O_2 = 2H_2O + O_2$. They also showed that the ratio (alcohol oxidised)/(Fe^{++} oxidised) could be greater than unity.

More recently, Baxendale, Evans and Park,[5] in a few brief experiments have shown that the active agent—the hydroxyl radical, ·OH—concerned in initiating the chain polymerisation of olefines by hydrogen peroxide, is identical with that which effects the rapid oxidation of glycollic acid.

[1] Waters, *The Chemistry of Free Radicals* (Oxford, 1946), pp. 247-52.
[2] (*a*) Fenton, *J. Chem. Soc.*, 1899, **75**, 1; (*b*) Fenton, *ibid.*, 1894, **65**, 899; 1895, **67**, 775; (*c*) Fenton, *ibid.*, 1900, **77**, 69.
[3] Wieland and Franke, *Annalen*, 1927, **457**, 1.
[4] Goldschmidt and Pauncz, *ibid.*, 1933, **502**, 1.
[5] Baxendale, Evans and Park, *Trans. Farday Soc.*, 1946, **42**, 155.

We have confirmed that the simple water-soluble alcohols are all oxidised rapidly by Fenton's reagent: the primary alcohols yield aldehydes which are further oxidised, at comparable rates, by exactly the same mechanism. By adopting the technique of adding a known quantity of hydrogen peroxide, or sodium persulphate solution to a mixture of an alcohol and a ferrous salt, so that only a portion of the latter was oxidised, and then, when reaction had ceased, estimating iron colorimetrically (Fe^{+++} by thiocyanate and Fe^{++} by $\alpha\alpha'$-dipyridyl) we have been able both to establish the mechanism of the oxidation process, and to compare the velocity constants for the oxidation of different alcohols. This simple procedure is one which we hope to extend to the study of the oxidation of organic compounds of other types. As yet our experiments have been carried out only at room temperature (*ca.* 18° c.) in dilute aqueous solutions of known *p*H, the majority of them being conducted in the presence of sufficient sulphuric acid to maintain *p*H = 1, at which point the efficiency of alcohol oxidation apparently reaches a maximum.

Persulphate Oxidation—

The Simple Reaction Mechanism—

The reaction sequence:

Chain starting:

$$Fe^{++} + S_2O_8^{=} \xrightarrow{k_1} Fe^{+++} + \cdot SO_4^{-} + (:SO_4)^{=} \qquad (1)$$

Chain ending:

$$Fe^{++} + \cdot SO_4^{-} \xrightarrow{k_2} Fe^{+++} + (:SO_4)^{=} \qquad (2)$$

Oxidation Chain:

$$\begin{cases} \cdot SO_4^{-} + R\text{—}CH_2OH \xrightarrow{k_3} HSO_4^{-} + R\text{—}\dot{C}H\text{—}OH & (3) \\ R\text{—}\dot{C}H\text{—}OH + S_2O_8^{=} \xrightarrow{k_4} R\text{—}CHO + HSO_4^{-} + \cdot SO_4^{-} & (4) \end{cases}$$

accords quite well with experimental measurements for the oxidation of alcohols in concentrations up to 20 % with 0·01 N. sodium persulphate in the presence of an excess of ferrous ammonium sulphate.

From the above equations we can easily derive the expressions

$$[SO_4^{-}] = k_1/k_2\,[S_2O_8^{=}]\,;\quad [R\text{—}\dot{C}H\text{—}OH] = \frac{k_1k_3}{k_2k_4}[R\text{—}CH_2OH]$$

and

$$\frac{-\,d[RCH_2OH]}{dt} = k_3k_1/k_2[R\text{—}CH_2OH]\,.\,[S_2O_8^{=}]$$

$$\frac{-\,d[Fe^{++}]}{dt} = 2k_1[Fe^{++}]\,.\,[S_2O_8^{=}]$$

whence we may deduce that, if this simple chain mechanism holds,

$$\frac{-\,d[R\text{—}CH_2OH]}{-\,d[Fe^{++}]} = \frac{k_3}{2k_2}\,\frac{[R\text{—}CH_2OH]}{[Fe^{++}]} \qquad (A)$$

$$\frac{-\,d[S_2O_8^{=}]}{-\,d[Fe^{++}]} = \tfrac{1}{2} + \frac{k_3}{2k_2}\,.\,\frac{[R\text{—}CH_2OH]}{[Fe^{++}]} \qquad (B)$$

$$\frac{-\,d[S_2O_8^{=}]}{-\,d[RCH_2OH]} = 1 + \frac{k_2}{k_3}\,.\,\frac{[Fe^{++}]}{[R\text{—}CH_2OH]} \qquad (C)$$

If calculations are made in *equivalents* throughout, the right-hand sides of equations (A) and (B) have to be multiplied by 2. Equation (C) is not altered.

Consequently, if our interpretation of the reaction-mechanism is correct, the ratios $-\,d(RCH_2OH)/-\,d(Fe^{++})$, etc., should all be independent of the rate of addition of the persulphate to the reaction mixture. This is indeed the case: the same amount of ferrous iron is oxidised whether the oxidiser is added dropwise or rapidly to the alcohol-ferrous salt mixture. However, if a ferrous salt is added to an alcohol-hydrogen peroxide, or

to an alcohol-persulphate mixture (as in some of Wieland's experiments) then the amount of alcohol which is rapidly oxidised is *not* reproducible, but depends on the rate of addition of the ferrous salt. Under these conditions we may frequently approach the limit $[Fe^{++}] \sim 0$, for which the ratio $-d[RCH_2OH]/-d[Fe^{++}]$ becomes infinity.

Nevertheless, this reverse procedure of adding a ferrous salt solution dropwise to a reactant-peroxide mixture is, preparatively, the most efficient method of oxidising any substance with Fenton's reagent. Chain-lengths of many hundreds can be attained for alcohol oxidation in this way.

If, however, we adopt the less efficient, but reproducible, oxidation procedure, and allow sufficient time for the complete destruction of the

FIG. 1. FIG. 2.

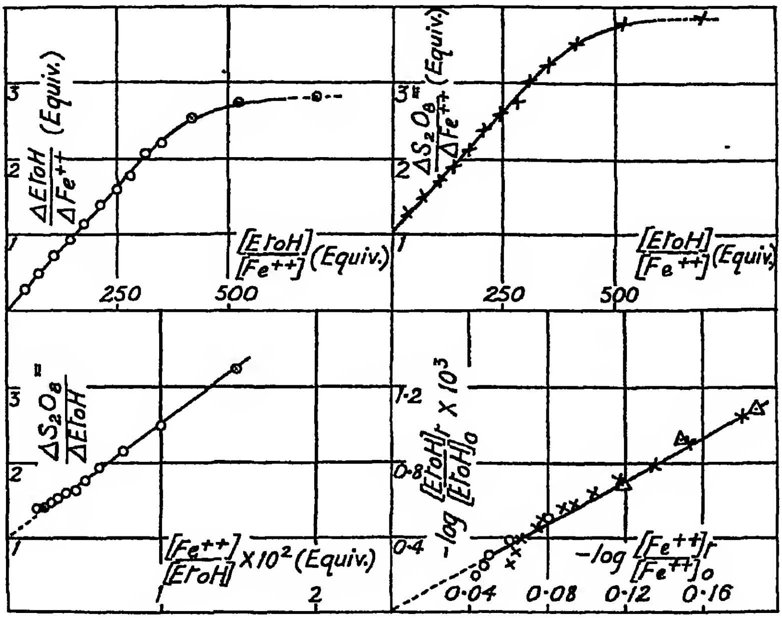

FIG. 3. FIG. 4.

FIG. 1-4.—Oxidation of EtOH with $Na_2S_2O_8$ in 0·1 N. H_2SO_4.

FIG. 1-3.—Each mixture contained 10 ml. of 0·1 N. ferrous ammonium sulphate, and was treated with 5 ml. of 0·1 N. persulphate, the total vol. being kept at 50 ml. in each case.

FIG. 4.—The integrated expression (D).
10 ml. of 0·1 N. Fe^{++} in each case.
Points ⊙ 2·5 ml. of 0·1 N. persulphate.
× 5·0 ml. ,,
△ 10·0 ml. ,,

persulphate or peroxide (only a few seconds in the case of hydrogen peroxide itself), keeping Fe^{++} in excess, then, to a first approximation we can take

$$\frac{-d[R{-}CH_2OH]}{-d[Fe^{++}]} = \frac{\Delta R{-}CH_2OH}{\Delta Fe^{++}} = \frac{\Delta S_2O_8^{-} - \Delta Fe^{++}}{\Delta Fe^{++}}, \text{ etc.,}$$

where $-\Delta Fe^{++} = +\Delta Fe^{+++}$ = ferric ion formed and $-\Delta S_2O_8^{-}$ = persulphate added, and can correlate these with the *initial* concentrations of alcohol and Fe^{++} in our solutions.

Fig. 1-3 show that equations (A), (B), and (C) hold quite satisfactorily

for the persulphate oxidation of ethyl alcohol at concentrations up to 150 g./l., though at higher alcohol concentrations a different chain-ending evidently comes in to limit the value of the $\Delta R—CH_2OH/\Delta Fe^{++}$ ratio.

It is more accurate, however, to use equations (A), etc., in their integrated forms:

$$\log \frac{[R—CH_2OH)_t}{[R—CH_2OH)_0} = \frac{k_3}{2k_2} \log \frac{(Fe^{++})_t}{(Fe^{++})_0} \quad . \quad . \quad . \quad (D)$$

where $[R—CH_2OH]_t$ and $(Fe^{++})_t$ are the *final* concentrations of alcohol and ferrous ion, and $[S_2O_8^{-}]_t$ is of course zero.

Fig. 4 shows that data obtained by adding different amounts of persulphate to alcohol-ferrous ammonium sulphate mixtures all lead to the same value for the ratio k_3/k_2.

Hydrogen Peroxide Oxidation.

1.—**The Simple Reaction Mechanism.**—An exactly similar set of equations to (1) to (4) can be set up for oxidation with hydrogen peroxide in acid solution, merely by replacing ·OH for the sulphate radical-ion ·O—SO_3^-, for under these circumstances the decomposition of the hydro-peroxide anion by ferric salts: $Fe^{+++} + HO_2^- \rightarrow Fe^{++} +$ HO—O·, which leads to "catalase" decomposition[6] becomes negligible. Our experiments have shown that hydrogen peroxide is a more powerful oxidiser than persulphate, giving, for ethyl alcohol, a ratio $k_3/k_2 = 2{\cdot}0$ instead of 0·006 at similar concentrations.

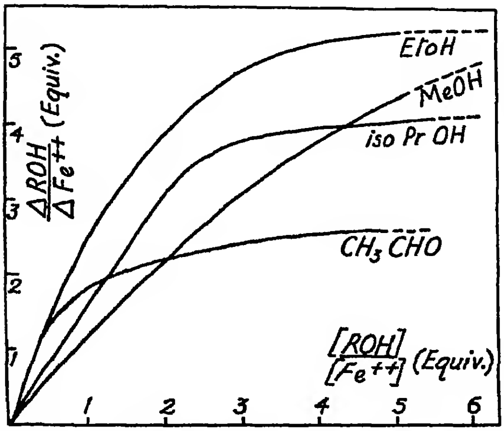

FIG. 5.—Oxidation with hydrogen peroxide.
10 ml. of 0·1 N. Fe^{++} in 50 ml. of each mixture.
·Oxidation with 10 ml. of 0·05 N. H_2O_2.

Even at low alcohol concentrations, however, there is a departure from the linear relationships corresponding to eqn. (A)-(D), and though considerably more than 50 % of the hydrogen peroxide reacts with the alcohol, the efficiency of alcohol oxidation tends to fall off, and apparently approaches a definite upper limit at high alcohol concentrations.

The deviation from the linear relationships are due to at least two causes: e.g. (*a*) the occurrence of other chain-ending reactions, and (*b*) consecutive oxidation of aldehyde to carboxylic acid.

Fig. 5 shows that acetaldehyde (initially peroxide-free) behaves in a similar manner to ethyl alcohol, and that at low concentrations *iso*propyl alcohol, which yields acetone which is not further oxidised, satisfies the simple chain-mechanism quite satisfactorily.

2. **Alternative Chain-endings.**—Fig. 5 indicates that at high alcohol concentrations the alcohol-radical concentration [R—ĊH—OH] cannot continue to increase linearly with $[R—CH_2OH]$ in accordance with the relationship

$$[R—\dot{C}HOH] = \frac{k_1k_3}{k_2k_4}[R—CH_2OH].$$

[6] Haber and Weiss, *Proc. Roy. Soc.*, *A*, 1934, **147**, 332; *B*, 1945, **119**, 47.

Possible explanations of this are the following.

(i) *Oxidation of the alcohol, or of its radical by ferric ions,*

e.g. $$R{-}\dot{C}HOH + Fe^{+++} \longrightarrow R{-}CHO + Fe^{++} + H^{+}.$$

Oxidations of this type were postulated in the original schemes of Haber and Willstätter[7]. Table I, however, shows that they do not occur, since the mean consumption ratio—ΔEtOH/—ΔFe^{++} is not significantly altered by adding a large excess of ferric sulphate.

TABLE I

Total volume = 55 ml. in each case. Fe^{++} estimated with dipyridyl: 10 ml. of 0·1 N. Fe^{++} and 10 ml. of 0·1 N. H_2O_2 in each case. The ratios are given in equivalents throughout.

EtOH/Fe^{++}	1·0	1·0	2·5	2·5
ml. M./2 Fe^{+++} added	—	10	—	10
ΔEtOH/ΔFe^{++} found	2·84	2·51	4·93	4·60

(ii) *Chain-ending by reaction between alcohol and hydroxyl radicals,*

e.g. $$R{-}\dot{C}HOH + \cdot OH \xrightarrow{k_5} R{-}CHO + H_2O. \quad . \quad . \quad (5)$$

Under the conditions of the experiments, in which $[Fe^{++}]$ is always present in much higher concentration than that of either of the radicals, it is exceedingly improbable that (5) should occur extensively in preference to (2).

However, if we consider that (5) replaces (2) as the chain-ending, but that at high alcohol concentrations (5) occurs much less frequently than either (3) or (4), then approximately

$$\frac{-\,d[EtOH]}{-\,d[Fe^{++}]} \text{ should become } 0{\cdot}5 + \left(\frac{k_4 k_3}{2k_1 k_5} \times \frac{[EtOH]}{[Fe^{++}]}\right)^{\frac{1}{2}}.$$

This fails to account for one of the distinctive features of the oxidation at high alcohol concentrations—the variation of the consumption ratio with the amount of oxidising agent used.

If, however, (5) occurs in place of (4)—i.e. if we are not dealing with a chain oxidation but with a two-stage oxidation of alcohol by hydroxyl radicals, then we should find the relationship

$$\frac{-\,d[H_2O_2]}{-\,d[EtOH]} = 2 + \frac{k_2}{k_3}\,\frac{[Fe^{++}]}{[EtOH]} \quad .$$

in place of that of eqn. (C). That this condition does not hold has been shown graphically, from experiments, though indeed it is obvious since more alcohol than iron can be oxidised by Fenton's reagent.

Hence chain-ending (5) can be discounted as a major reaction.

(iii) *Disproportionation of alcohol radicals,*

i.e. $$2R{-}\dot{C}H{-}OH \xrightarrow{k_6} R{-}CHO + R{-}CH_2OH \quad . \quad . \quad (6)$$

Clearly this will tend to become more and more probable the higher the alcohol concentration. Moreover reactions of this type account most satisfactorily for glycol-splitting by Fenton's reagent.[8, 9] For a reaction sequence involving equations (1), (3), (4) and (6)

$$\frac{-\,d[R{-}CH_2OH]}{-\,d[Fe^{++}]} = k_4 \,.\, \left(\frac{[H_2O_2]}{k_1 k_6 [Fe^{++}]}\right)^{\frac{1}{2}} \quad . \quad . \quad (D)$$

—a relationship which is independent of the alcohol concentration but

[7] Haber and Willstätter, *Ber.*, 1931, **64**, 2844.
[8] Waters, *Trans. Faraday Soc.*, 1946, **42**, 185.
[9] Waters, *Nature*, 1946, **158**, 380.

dependent upon that of the oxidising agent. This does seem to approximate more closely to the facts than either of the hypotheses (i) or (ii). The true state of affairs, in which both reactions (2) and (6) must be considered as chain-ending processes, contains too many variables for complete analysis.

The Effect of Dilution.

It has been noticed that the mean consumption ratio,

$$\Delta R{-}CH_2OH/\Delta Fe^{++}$$

decreases if the initial reaction mixture is diluted with water or acid. Tables II and III show typical results.

None of the eqn. (1) to (5) can account for this change, for they are all first-order processes with respect to alcohol, iron and oxidiser individually, and so lead to ratios (A) to (C), which are functions of relative, and not absolute, concentrations of reactants.

TABLE II

DILUTION EFFECT FOR PERSULPHATE OXIDATION

Reaction mixture = 10 ml. 0·2 N. Fe^{++}; 5 ml. 3 M. EtOH; 10 ml. 0·1 N. $Na_2S_2O_8$.
Dilution made with 1 N. H_2SO_4.

Final volume (ml.)	25	50	75	100	125	150
$(S_2O_8^{=})$ at t_0 (N.) .	0·04	0·02	0·0133	0·01	0·008	0·0067
$\dfrac{\Delta EtOH}{\Delta Fe^{++}}$ (Equiv.) .	0·20	0·16	0·136	0·10	0·095	0·067

TABLE III

DILUTION EFFECT FOR HYDROGEN PEROXIDE OXIDATION

(*A*) *At High Alcohol Concentrations.*

Reaction mixture = 5 ml. 0·1 N. Fe^{++}; 6 ml. 5 M. EtOH; 5 ml. 0·05 N. H_2O_2
Dilution made with 0·2 N. H_2SO_4.

For series (i) $[EtOH]/[Fe^{++}]$ = 60; for series (ii) 120 equiv.

Final vol. (ml.) . .	20	30	50	100	140
$(H_2O_2$ at t_0 (N.) .	0·0125	0·0083	0·005	0·0025	0·0018
(i) $\dfrac{\Delta EtOH}{\Delta Fe^{++}}$ (equiv.) .	6·49	5·99	4·22	2·35	1·54
(ii) ,, .	6·75	6·14	4·45	2·56	1·64

(*B*) *At Low Alcohol Concentrations.*

Reaction mixture = 5 ml. 0·1 N. Fe^{++}; 6 ml. M./12 EtOH; 5 ml. 0·05 N. H_2O_2.
Dilution made with 0·2 N. H_2SO_4.

For series (i) $(EtOH)/(Fe^{++})$ = 1·0; for series (ii), 2·0 equiv.

Final vol. (ml.) . .	20	40	60	100
$[H_2O_2]$ at t_0 (N.) . .	0·0125	0·00625	0·0042	0·0025
(i) $\dfrac{\Delta EtOH}{\Delta Fe^{++}}$ (equiv.) .	1·97	1·54	1·31	0·85
(ii) ,, .	2·85	2·53	1·94	1·22

However, as one of us has frequently pointed out [10, 1] the reaction between an alcohol molecule and a hydroxyl radical may be reversible,

[10] Waters, *Trans. Faraday Soc.*, 1941, 37, 779.

although the equilibrium is certainly very much in the direction of oxidation of the alcohol. Thus for hydrogen peroxide oxidation we should write, in place of (3), the equilibrium

$$R{-}CH_2OH + \cdot OH \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} R{-}\dot{C}HOH + H{-}OH. \qquad (3')$$

For persulphate oxidation the reverse reaction is identical with that of (3′) above, and involves production of a little free hydroxyl. Consequently the persulphate and peroxide reactions cannot be entirely differentiated from one another. It is indeed possible that the sulphate radical-ion, $\cdot SO_4^-$ (i.e. $\cdot\ddot{O}{-}SO_2{-}\ddot{O}{:}^-$) may, in a similar way be converted to hydroxyl radical, by the occurrence of $\cdot SO_4^- + H_2O \rightleftharpoons HSO_4^- + \cdot OH$

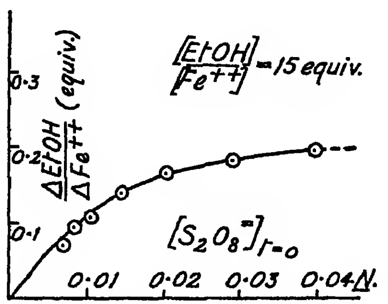

FIG. 6.—Dilution effect with $Na_2S_2O_8$. Reagents, 10 ml. 0·2 N. Fe^{++}; 10 ml. of 0·1 N. $Na_2S_2O_8$.

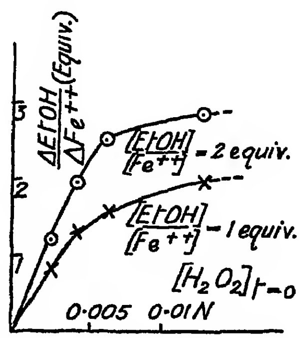

FIG. 7.—Dilution effect with hydrogen peroxide. Reagents, 5 ml. of 0·1 N. Fe^{++}; 5 ml. of 0·05 N. H_2O_2.

though the great difference between the values of the ratio k_3/k_2 for the persulphate and peroxide oxidations indicates that the reactions of type (3) are not the same in both cases.

If we introduce a reversible reaction (3′) into our kinetic equations then the net effect is that at high water concentrations (high dilution) we should tend to re-form much of our alcohol from alcohol radicals, with a consequent decrease of the efficiency of the oxidation process. The full kinetic expression for this is

$$\frac{-\,d[R{-}CH_2OH]}{-\,d[Fe^{++}]} = \frac{k_3}{2k_2} \cdot \frac{[R{-}CH_2OH]}{[Fe^{++}]} \cdot \left(\frac{k_4/k_3'[H_2O_2]}{1 + k_4/k_3'[H_2O_2]}\right) \qquad (E)$$

If the term k_4/k_3' . $[H_2O_2]$ is large, i.e. if $k_4 \gg k_3'$ or if the concentration of the oxidising agent is high, then equation (E) reduces to equation (A). At very low concentrations of the oxidising agent, however, the consumption ratio should become proportional to the concentration of the oxidising agent. Fig. 6 and 7 show that this is valid. Moreover, as shown by Table IV, we can counteract the "dilution effect" quite simply by

TABLE IV

COMPENSATION FOR DILUTION EFFECT BY USING A CONSTANT CONCENTRATION OF OXIDISER.

Reaction mixture = 10 ml. 0·1 N. Fe^{++}; 3 ml. EtOH; pH kept constant (= 1) with H_2SO_4. $(Na_2S_2O_8)$ maintained at t_0 as N./80.

Final vol. (ml.)	20	40	60	80	100	120
$S_2O_8^=$ used (ml. of N./20)	5	10	15	20	25	30
$\frac{\Delta EtOH}{\Delta Fe^{++}}$ equiv.	0·97	1·09	1·03	1·04	1·00	1·06

increasing the concentration of our oxidising agent proportionally to the dilution of the reaction mixture.

The Nature of the Alcohol Radical.

The primary reaction (3) between a hydroxyl radical and an alcohol molecule can be written either as (*a*) or as (*b*):

$$(a)\ R—CH_2—OH + \cdot OH \rightleftharpoons R—\dot{C}H—OH + H—OH \qquad (cf.\ 3)$$
$$(b)\ R—CH_2—OH + \cdot OH \rightleftharpoons R—CH_2—O\cdot + H—OH.$$

The exact formulation of the alcohol radical is a moot point particularly since the possibility of tautomerism must be conceded.[11] Reaction (*a*) accords with the fact that in isolated alcohol molecules the C—H bond is weaker than the O—H bond; only reaction (*b*) satisfactorily explains glycol fission.

Formulation (*a*) has been used in the preceding pages because it is difficult to conceive that a monovalent oxygen radical, $R—CH_2—O\cdot$ could attack either molecular hydrogen peroxide, or the persulphate anion, and surrender an additional electron, for this would give an oxygen cation, $R—CH_2—O^+$. On the contrary, $R—CH_2—O\cdot$ should, like hydroxyl, be an oxidising agent. A trivalent carbon radical, $R—\dot{C}H—OH$, however, can easily lose one more electron to give a cation which is the proton adduct of an aldehyde:

$$R—\dot{C}H—OH + \cdot OH \longrightarrow R—\overset{+}{C}H—OH + (:OH)^- \qquad (cf.\ 5)$$
$$R—\overset{+}{C}H—O—H \rightleftharpoons R—CH{=}O + H^+,$$

or, alternatively, it could add on hydroxyl radical to give the hydrated form of the aldehyde

$$R—\dot{C}H—OH + \cdot OH \longrightarrow R—CH(OH)_2 \rightleftharpoons R—CH{=}O + H_2O.$$

Reactions in which single electrons are given up to, or hydroxyl radicals abstracted from, hydrogen peroxide molecules can be formulated similarly, without difficulty, and these certainly do occur, as process (4) in the simple chain mechanism.

On the other hand, the " dilution effect " is most simply represented as

$$R—CH_2—O\cdot + H—OH \rightleftharpoons R—CH_2—O—H + \cdot OH.$$

We therefore conclude that, in water, the alcohol radical is a tautomeric system in which the trivalent carbon form predominates.

In view of Wieland's evidence of the oxidation of aldehydes only in their hydrated forms, $R—CH(OH)_2$,[12] we are faced with the same alternatives concerning the structure of the aldehyde radical. The structure $R—\dot{C}{=}O$ is an improbable one.

Relative Rates of Oxidation of Homologous Alcohols.

Eqn. (A) and (D) allow us to evaluate the ratio k_3/k_2. Consequently if we take a series of alcohols, and oxidise them at the same degree of dilution, we can get *relative* values of k_3, the velocity constant for the initial abstraction of hydrogen from the alcohol molecule either by free hydroxyl or by the sulphate radical-ion. Comparative rates of addition of hydroxyl radicals to double bonds have been measured by Baxendale, Evans and Park[8] in exactly the same way, and are noticeably higher than our rates of oxidation.

Table V gives values for these constants for persulphate oxidation, under conditions in which equation (D) is valid.

[11] Waters, *J. Chem. Soc.*, 1946, 1153.
[12] Wieland and Richter, *Annalen*, 1932, 495, 284.

The order *iso*-Propyl > *n*-Propyl = Ethyl > Methyl is the expected order for electron release at the C—H bond of the carbinol group, since alkyl substituents will tend to increase the electron-density at this carbon atom by their general inductive effect $\overset{+\longrightarrow}{CH_3\text{—}}CH_2OH$.

In the case of oxidation with hydrogen peroxide, our experiments indicate that the relative rates of oxidation of the different alcohols change with changing concentration ratios (cf. Fig. 5). Alternative chain endings,

TABLE V

RELATIVE VELOCITY OF OXIDATION OF ALCOHOLS BY THE SO_4^- RADICAL-ION.

Alcohol	CH_3OH	C_2H_5OH	n—C_3H_7OH	*iso*-C_3H_7OH
k_3/k_2	0·0022	0·0062	0·0061	0·0089

and, more particularly, the consecutive oxidations of aldehydes to acids vitiate attempts to determine accurate relative velocity constants. Table VI, however, gives one set of relative figures made at one (identical) dilution at which equation (A) is still approximately true.

Even under these conditions (actually taking equiv. substance/equiv. Fe^{++} = 1) the figures for the oxidations of the primary alcohols are those for oxidation of (alcohol + aldehyde). For the persulphate oxidations the ratios k_3/k_2 are so low that we can use high initial (alcohol)/(Fe^{++})

TABLE VI

RELATIVE VELOCITY OF OXIDATION OF ALCOHOLS AND ALDEHYDES WITH HYDROXYL RADICAL

Substance	CH_3OH	C_2H_5OH	n-C_3H_7OH	*iso*-C_3H_7OH	CH_2O	CH_3—CHO
k_3/k_2	1·14	2·05	1·30	1·77	1·04	1·08

ratios, and minimise errors due to oxidation of the small percentage of aldehyde which may be formed.

The fact that the relative velocity constants for the alcohol and the aldehyde oxidations are so comparable is further evidence in favour of the view that the aldehydes react in their hydrated forms, R—$CH(OH)_2$.

Summary.

The mechanism of the oxidation of alcohols and of aldehydes with sodium persulphate, and with hydrogen peroxide, in the presence of an excess of a ferrous salt has been shown, by quantitative measurements, to be as follows:

Chain starting:

$$Fe^{++} + HO\text{—}OH \longrightarrow Fe^{+++} + \cdot OH + (:OH)^-.$$

Reaction chain:

$$RCH_2OH + \cdot OH \rightleftharpoons R\text{—}\dot{C}HOH + H\text{—}OH \text{ (reversible)}$$

$$R\text{—}\dot{C}HOH + HO\text{—}OH \longrightarrow R\text{—}CHO + \cdot OH + H_2O$$

Chain ending at low alcohol concentrations:

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + (:OH)^-$$

Chain ending at high alcohol concentrations:

$$2R\text{—}\dot{C}HOH \longrightarrow R\text{—}CHO + R\text{—}CH_2OH \text{ (disproportionation)}$$

It is possible, by this reaction, to determine the relative rates of hydrogen atom removal from different alcohols or aldehydes.

Résumé.

Des mesures quantitatives ont montré qu'il est possible de représenter le mécanisme de l'oxydation des alcools et des aldéhydes par le persulfate de sodium et par l'eau oxygénée, en présence d'un excès de sel ferreux, de la façon suivante :

Commencement de la chaîne :

$$Fe^{++} + HO—OH \longrightarrow Fe^{+++} + OH + (:OH)^-$$

Réactions de la chaîne :

$$RCH^2OH + \cdot OH \rightleftharpoons R\dot{C}HOH + H—OH \text{ (réversible)}$$
$$R—\dot{C}HOH + HO—OH \longrightarrow RCHO + \cdot OH + H_2O$$

Terminaison de la chaîne aux faibles concentrations d'alcool :

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + (:OH)^-$$

Terminaison de la chaîne aux fortes concentrations d'alcool :

$$2\ R—\dot{C}HOH \longrightarrow R—CHO + R—CH_2OH \text{ (dismutation)}$$

Cette réaction permet de déterminer les vitesses relatives auxquelles un atome d'hydrogène est retiré de différents alcools ou aldéhydes.

Zusammenfassung.

Quantitative Messungen ergeben den folgenden Reaktionsmechanismus für die Oxydation von Alkoholen und Aldehyden mit Natriumpersulfat oder Wasserstoffperoxyd in der Gegenwart von überschüssigem Ferrosalz :

Kettenanfang

$$Fe^{++} + HO—OH \longrightarrow Fe^{+++} + \cdot OH + (:OH)^-$$

Kette

$$RCH_2OH + \cdot OH \rightleftharpoons R\dot{C}HOH + H—OH$$
$$R—\dot{C}HOH + HO—OH \longrightarrow RCHO + \cdot OH + H_2O$$

Kettenendigung bei niedrigen Alkohol konzentrationen

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + (:OH)^-$$

Kettenendigung bei hohen Alkohol konzentrationen

$$2\ R—\dot{C}HOH \longrightarrow R—CHO + R—CH_2OH \text{ (Disproportionation).}$$

Durch diese Reaktion ist es möglich die relativen Geschwindigkeiten der Entfernung von Wasserstoffatomen in verschiedenen Alkoholen zu messen.

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ON THE NATURE OF THE "ACTIVE" OXALIC ACID.

BY JOSEPH WEISS.

Received 21st August, 1947.

Oxalic acid if treated with an insufficient amount of certain oxidising agents (permanganate, persulphate, etc.) acquires an increased reducing power which manifests itself, e.g. in the ready reduction of mercuric chloride to calomel. This "activation" of oxalic acid was first observed by Dhar [1] and was subsequently studied by Oberhauser *et al.*[2] and Wieland

[1] Dhar, *J. Chem. Soc.*, 1918, 111, 690 ; *J. Indian Chem. Soc.*, 1928, 5, 203.
[2a] Oberhauser and Hensinger, *Ber.*, 1928, 61, 521.
[2b] Oberhauser and Schormüller, *Ann. Chem.*, 1929, 470, 111.

and Zilg.[3] The reaction may be also of some biological interest as Thunberg [4] has found that oxalates can be "activated" to reduce Methylene Blue by certain substances from the seeds of *Malvacea* plants.

It has been suggested at various times that the "activated" oxalic acid is due to the formation of glyoxalic or formic acid or to some new form of oxalic acid. These views have now been abandoned.[3] Similarly, Wieland's suggestion [3] that one is dealing with an "excited" form of oxalic acid is clearly incompatible with the facts. Abel [5] and others have suggested that the semi-oxidised oxalate-ion ($C_2O_4^-$) is the cause of this peculiar behaviour which, however, has been questioned by other workers.[6]

In this paper an attempt has been made to sketch a mechanism of these reactions on a semi-quantitative basis and to clarify some points especially those with regard to the supposedly long life-time of the "active" oxalic acid which is observed under certain conditions.

(1) Activation by the System Hydrogen peroxide-Ferrous Salt.

The H_2O_2-Fe^{II} system offers certain advantages because it is known with some certainty that it produces OH radicals.[7a, 7b, 8] Firstly some experiments are reported on the oxidation of oxalic acid (in the absence of $HgCl_2$). The results, which are similar to those obtained by Wieland and Zilg [3] are represented in Fig. 1. This shows the relation between the ratio of the equivalents of oxalic acid oxidised per one equivalent of ferrous salt

$$\left(\bar{n}_1 = \frac{2\Delta(H_2C_2O_4)}{\Delta(Fe^{II})} = \left|\frac{\Delta(CO_2)}{\Delta(Fe^{II})}\right|\right)$$

at different initial concentrations of ferrous salt (at constant initial concentrations of the other reactants). It is obvious that one is dealing with a chain reaction where $\bar{n}_1$ represents the mean "chain length."

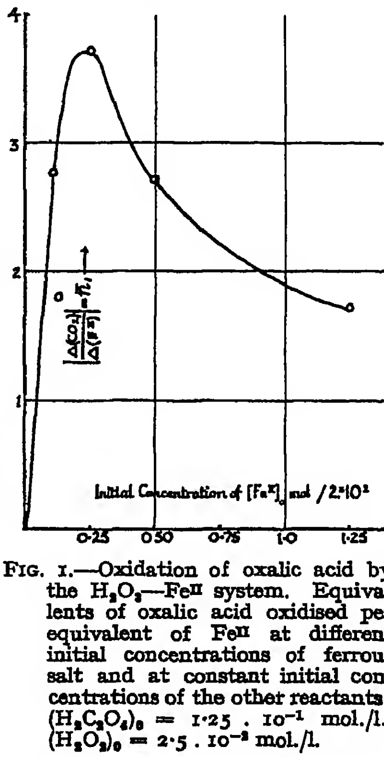

FIG. 1.—Oxidation of oxalic acid by the H_2O_2—Fe^{II} system. Equivalents of oxalic acid oxidised per equivalent of Fe^{II} at different initial concentrations of ferrous salt and at constant initial concentrations of the other reactants: $(H_2C_2O_4)_0 = 1{\cdot}25 \cdot 10^{-1}$ mol./l., $(H_2O_2)_0 = 2{\cdot}5 \cdot 10^{-2}$ mol./l.

If mercuric chloride is added to the system oxalic acid and H_2O_2—Fe^{II}, a rapid formation of calomel takes place. Wieland and Zilg [3] have reported that equivalent amounts of $\Delta(CO_2)$ and $\Delta(HgCl)$ are formed. We were able to confirm their result as will be seen from Fig. 2*a*.

The mean consumption ratio $\bar{n}_2 = \left|\frac{\Delta(HgCl)}{\Delta(Fe^{II})}\right|$—after a rapid increase—decreases with increasing initial concentration of $(Fe^{II})_0$ (Fig. 2*b*) while the total amount of calomel produced varies only slightly at medium $(Fe^{II})_0$ (Fig. 2*c*). The reactions come to an end when all the Fe^{II}- salt has been transformed to the ferric stage. This feature which seemed unaccountable to Wieland [3] follows immediately from a chain mechanism with Fe^{3+} initiating the chains.

[3] Wieland and Zilg, *Ann. Chem.*, 1937, **530**, 257.
[4] Thunberg, *Arch. Physiol.*, 1928, **54**, 6.
[5] Abel, *Z. Elektrochem.*, 1937, **43**, 629.
[6] Weber, *Z. physik. Chem. B*, 1934, **25**, 363.
[6a] Weber, *ibid.*, *A*, 1935, **172**, 459.
[7a] Haber and Weiss, *Proc. Roy. Soc. A*, 1934, **147**, 332.
[7b] Weiss, *J. Physic. Chem.*, 1937, **41**, 1107.
[8] Baxendale, Evans and Park, *Trans. Faraday Soc.*, 1946, **42**, 155.

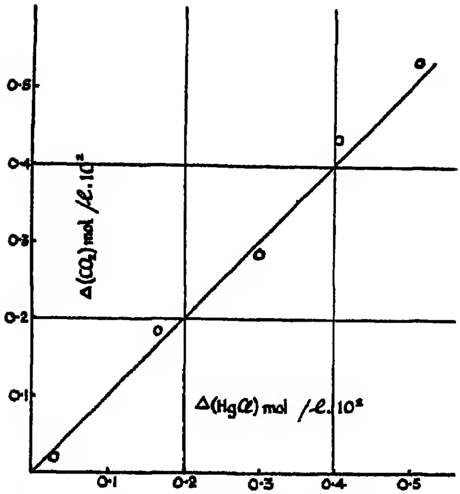

FIG. 2(*a*).—Relation between the amounts of calomel and CO_2 formed at different initial concentrations of ferrous salt and constant initial concentrations of $(H_2C_2O_4)_0 = 8{\cdot}33 . 10^{-3}$ mol./l., $(H_2O_2)_0 = 1{\cdot}66 . 10^{-3}$ mol./l., $(HgCl_2)_0 = 3{\cdot}10^{-2}$ mol./l.

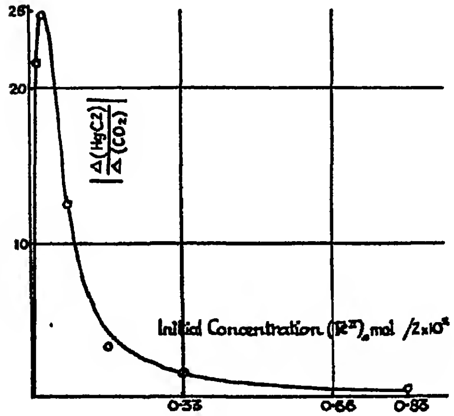

FIG. 2(*b*).—Mean consumption ratio $\left|\frac{\Delta(HgCl)}{\Delta(Fe^{II})}\right|$ at different initial concentrations of ferrous salt at constant initial concentrations of $(H_2O_2)_0 = 1{\cdot}66 . 10^{-3}$ mol./l., $(H_2C_2O_4)_0 = 8{\cdot}33 . 10^{-3}$ mol./l., $(HgCl_2)_0 = 3 . 10^{-2}$ mol./l. (20° C., nitrogen atmosphere.)

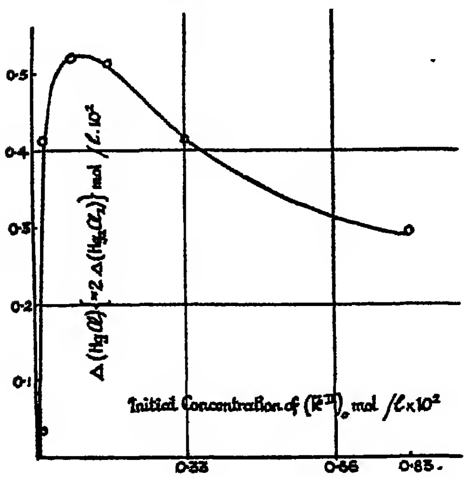

FIG. 2(*c*).—Calomel formed at different initial concentrations of ferrous salt, at constant initial concentrations of $(H_2C_2O_4)_0 = 8{\cdot}33 . 10^{-3}$ mol./l., $(H_2O_2)_0 = 1{\cdot}66 . 10^{-3}$ mol./l., $(HgCl_2)_0 = 3 . 10^{-2}$ mol./l. (20° C., nitrogen atmosphere.)

Fig. 3 shows the dependence of the amount of calomel formed on the initial concentration of hydrogen peroxide, the curve showing again an initial increase followed by a more or less marked decrease at higher $(H_2O_2)_0$, with the shape of the curves governed largely by $(Fe^{II})_0$. The dependence of the amount of

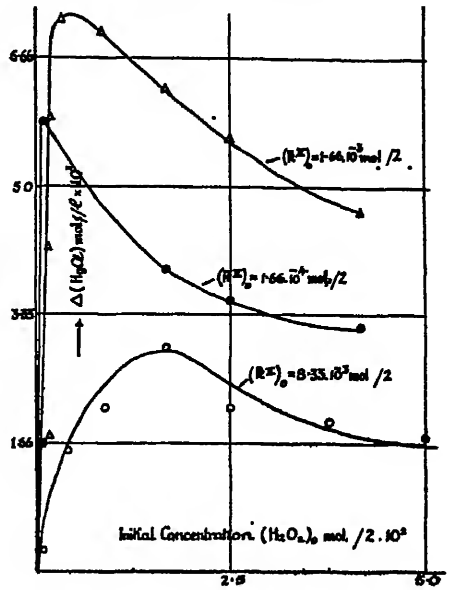

FIG. 3.—Calomel formed at different initial concentrations of hydrogen peroxide for three different initial concentrations of $(Fe^{II})_0$ at constant initial concentrations of $(H_2C_2O_4)_0 = 8 \cdot 33 \cdot 10^{-2}$ mol./l., $(HgCl_2)_0 = 3 \cdot 10^{-2}$ mol./l. (20° C. nitrogen atmosphere.)

calomel on the initial concentration of mercuric chloride is shown in Table I for two different initial concentrations of $(Fe^{II})_0$ at constant initial concentrations of the other reactants.

TABLE I.

$(H_2C_2O_4)_0 = 8 \cdot 33 \cdot 10^{-2}$ mol./l. $\quad (H_2O_2)_0 = 1 \cdot 66 \cdot 10^{-2}$ mol./l.

Expt. No.	$(HgCl_2)_0$ Mol./l.	(1) $(Fe^{II})^*_0 = 1 \cdot 66 \cdot 10^{-3}$ mol./l.		(2) $(Fe^{II})^*_0 = 1 \cdot 66 \cdot 10^{-2}$ mol./l.		Ratio $\frac{\Delta(HgCl)_{(2)}}{\Delta(HgCl)_{(1)}}$.
		Δ HgCl formed mol./l. 10^3.	$\frac{\Delta(HgCl)}{(HgCl_2)_0} \cdot 10^2$.	Δ HgCl formed mol./l. 10^3.	$\frac{\Delta(HgCl)}{(HgCl_2)_0} \cdot 10^2$.	
1	0·03	0·25	0·83	1·0	3·33	4·0
2	0·06	0·58	0·97	2·16	3·60	3·60
3	0·09	0·95	1·05	3·33	3·70	3·70
4	0·15	1·47	0·98	6·41	4·28	4·28

Mechanism.

It is not attempted to give an exhaustive treatment of the reaction mechanism. The following relatively simple mechanism which is based on the previous work of Haber and Weiss [7a] and Weiss [7b] seems to account for most of the essential features:

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + OH \quad . \quad . \quad . \quad (1)$$
$$Fe^{2+} + OH = Fe^{3+} + OH^- \quad . \quad . \quad . \quad . \quad (2)$$
$$C_2O_4^{2-} + OH = C_2O_4^- + OH^- \quad . \quad . \quad . \quad . \quad (3)$$
$$C_2O_4^- + H_2O_2 = 2CO_2 + OH^- + OH. \quad . \quad . \quad (4)$$

* FERROUS SULPHATE.—The amount of calomel increases approximately proportional to $(HgCl_2)_0$ (columns 4 and 6) while the amounts at different $(Fe^{II})_0$ increase as $(Fe^{II})_0$ decreases, showing an almost constant ratio (column 7).

For the stationary state (of OH and $C_2O_4^-$) one obtains from the above system of equations the following differential equation for the chain length (consumption ratio) $n_{1(t)}$ at time t:

$$n_{1(t)} = \left|\frac{d(CO_2)}{d(Fe^{II})}\right| = \frac{k_3\,[C_2O_4^{2-}]_t}{k_2\,[Fe^{2+}]_t} \quad . \quad . \quad . \quad (5)$$

The mean consumption ratio $\bar{n}_1$ over a time interval $(0 \rightarrow t)$ is given by:

$$\bar{n}_1 = \left|\frac{\Delta(CO_2)}{\Delta(Fe^{II})}\right| = \left|\frac{\int_0^t \frac{d(CO_2)}{dt}dt}{\int_0^t -\frac{d(Fe^{II})}{dt}dt}\right| \quad . \quad . \quad . \quad (5a)$$

the evaluation of which requires the complete integration of the simultaneous differential equations.

If H_2O_2 and $H_2C_2O_4$ are present in relatively high concentrations one may introduce as a first approximation either their initial values or somewhat modified mean concentrations. The mean value of $[Fe^{2+}]$ can be introduced which then can be calculated from the equation:

$$[Fe^{2+}]_m = \frac{1}{t}\int_0^t [Fe^{2+}]_t\,dt \quad . \quad . \quad . \quad . \quad (6)$$

which under the simplifying assumptions discussed above leads to:

$$[Fe^{2+}]_m = \frac{1}{t}\int_0^t [Fe^{2+}]_0\,e^{-2k_1[H_2O_2]_m t}\,.\,dt$$

$$= \frac{[Fe^{2+}]_0}{2k_1[H_2O_2]_m t}\left\{1 - e^{-2k_1[H_2O_2]_m t}\right\} \quad . \quad (6a)$$

Thus one obtains:

$$\bar{n}_1 \sim \frac{k_3}{k_2}\frac{[C_2O_4^{2-}]_m}{[Fe^{2+}]_m} \propto \frac{(H_2C_2O_4)_0}{(Fe^{2+})_0} \quad . \quad . \quad . \quad (7)$$

This equation is confirmed qualitatively by Fig. 1 in the descending part of the curve. It is clear, however, that as the curve must start at the origin ($\bar{n}_1 = 0$ for $(Fe^{2+})_0 = 0$), there must be an initial rise which, however, corresponds to an essentially pre-stationary state and therefore is not covered by the above equations.

In a more detailed treatment, apart from reaction (2), other chain-breaking processes may have to be included, such as:

$$C_2O_4^- + OH = 2CO_2 + OH^- \quad . \quad . \quad . \quad . \quad (8)$$

and possibly also

$$C_2O_4^- + Fe^{2+} \rightleftharpoons C_2O_4^{2-} + Fe^{3+} + \text{energy}. \quad . \quad (9)$$

Reaction (9) should be exothermic in the forward direction: while oxalate is not oxidised by Fe^{3+} in the dark this reverse process takes place easily under influence of light.

In the presence of $HgCl_2$ in the solution the above scheme of reactions has to be supplemented. It appears to be sufficient to introduce the reactions:*

$$C_2O_4^- + Hg^{2+} = Hg^+ + 2CO_2 \quad . \quad . \quad . \quad . \quad (10)$$

$$Hg^+ + C_2O_4^{2-} = Hg + C_2O_4^- \quad . \quad . \quad . \quad . \quad (11)$$

$$Hg^{2+} + Hg = Hg_2^{2+} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

These reactions have been discussed previously by Cartledge [9] in connection with the photochemical reaction between $HgCl_2$ and oxalate (Eder's reaction). Taking these reactions into account one obtains for the stationary state for the ratio $n_{2(t)}$ the differential equation:

$$n_{2(t)} = \frac{d(Hg_2Cl_2)}{d(CO_2)} = \frac{k_{10}[Hg^{2+}][C_2O_4^{2-}]}{2k_{10}[Hg^{2+}][C_2O_4^{2-}] + 2k_4[H_2O_2][C_2O_4^{2-}]} \quad . \quad (13)$$

* It is left open to which extent Hg^{2+} or perhaps the undissociated $HgCl_2$ enters into the reaction mechanism.

[9] Cartledge, *J. Amer. Chem. Soc.*, 1941, 63, 906.

Under the assumption of:

$$k_4[H_2O_2] < k_{10}[C_2O_4^{2-}] \quad . \quad . \quad . \quad . \quad . \quad (14)$$

this gives

$$\frac{2d(Hg_2Cl_2)}{d(CO_2)} = \frac{d(HgCl)}{d(CO_2)} \sim 1 \quad . \quad . \quad . \quad . \quad (15)$$

in agreement with experiment (Fig. 2*a*).

The mean consumption ratio with regard to Fe^{II}, i.e. the mean chain length is given by:

$$\bar{n}_3 = \left|2\frac{\Delta(Hg_2Cl_2)}{\Delta(Fe^{II})}\right| = \frac{k_{10}[Hg^{2+}]_m[C_2O_4^{2-}]_m}{k_1[Fe^{2+}]_m[H_2O_2]_m} \quad . \quad . \quad (16)$$

which is confirmed as well as can be expected by the experiments reproduced by Fig. (2*b*) and (2*c*) and by Table I.

It has been reported by several authors that molecular oxygen exerts a strong inhibiting effect [2, 3] on the formation of calomel. In conformity with Cartledge,[9] this may be attributed to the reactions:

$$C_2O_4^- + O_2 = 2CO_2 + O_2^- \quad . \quad . \quad . \quad . \quad . \quad (17)$$
$$Hg^+ + O_2 = Hg^{2+} + O_2^- \quad . \quad . \quad . \quad . \quad . \quad (18)$$

which lead to the formation of HO_2 radicals ($O_2^- + H^+ \rightleftharpoons HO_2$) which on subsequent reaction with any of the reducing substances present can yield HO_2^- (i.e. hydrogen peroxide).

It is of some interest that molecular iodine also exerts a very strong inhibiting effect. This is presumably due to the reaction:

$$C_2O_4^- + I_2 = 2CO_2 + I + I^- \quad . \quad . \quad . \quad . \quad (19)$$

which is known from the photochemical reaction between oxalate and iodine [10a, 10b] and which competes with reaction (10) which initiates the formation of calomel.

In an experiment corresponding to the conditions of experiment 1 (2) in Table I it was found that a concentration of $(I_2) \sim 10^{-5}$ mol./l. was sufficient to reduce the amount of calomel to about half of the normal quantity. From this may be deduced that k_{19} (reaction (19)) should be about 1000 times greater than k_{10} (reaction (10)).

Reducing substances (e.g. hydroquinone) also exert a strong inhibiting effect.[3] This can be attributed to their competition for the OH radicals, thus inhibiting the formation of $C_2O_4^-$ according to reaction (3) or possibly also to a reaction with the $C_2O_4^-$ radicals leading to the formation of $C_2O_4^{2-}$.

2. Activation by Permanganate.

The action of potassium permanganate on oxalic acid at room temperature is a relatively slow process which occurs in steps. One of the important intermediate stages is represented by Mn^{3+} ions, which oxidise oxalate ions in a rapid reaction. This has been known since the earlier work of Skrabal.[11] More recently Launer [12] and Lidwell and Bell [13] have suggested that the $C_2O_4^-$ radical appears as an intermediate in this reaction. From the discussion in Part I it is to be expected, therefore, that permanganate "activates" oxalic acid similar to the H_2O_2- Fe^{II} system.

If permanganate is added to a dilute solution of (more than equivalent) oxalic acid the colour of the solution changes from violet to brown and then gradually fades away until it finally becomes colourless. If $HgCl_2$ is added from the start one does not observe any formation of calomel as long as the solution is violet or even during the early stages of the brown

[10a] Abel, Retter and Schmid, *Z. physik. Chem. A*, 1932, 163, 53.
[10b] Griffith, McKeown and Winn, *Trans. Faraday Soc.*, 1933, 29, 369, 386.
[11] Skrabal, *Z. anorg. Chem.*, 1904, 42, 1.
[12] Launer, *J. Amer. Chem. Soc.*, 1932, 54, 2597.
[13] Lidwell and Bell, *J. Chem. Soc.*, 1935, 1303.

coloration : only as the colour fades away calomel formation sets in. This fact does not seem to have been mentioned by previous investigators although this "induction period" is obviously of some importance for the mechanism of "activation."

From the discussion in Part I it is clear that no calomel will be formed if there is a sufficient amount of oxidising agent present in the solution which can react with the chain carriers e.g. $C_2O_4^-$, according to :

$$C_2O_4^- + Mn^{3+} = 2CO_2 + Mn^{2+} \quad . \quad . \quad . \quad . \quad (20)$$

and which thus may inhibit to a greater or lesser extent the chain reactions (10), (11), (12) leading to the formation of calomel. Consequently the formation of calomel does not even start until the amount of oxidising agent in the solution has reached a certain (critical) low level, which is governed by the competition between the reactions (10), (11) and (20) respectively.

This can be demonstrated by adding the $HgCl_2$ to the system $H_2C_2O_4$-$KMnO_4$ at different stages of decolorisation. The amount of residual oxidising agent

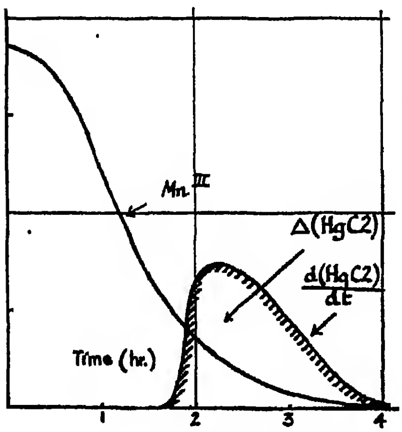

FIG. 4.—Schematic Representation of the Decrease of the oxidising agent (Mn^{III}) in the solution with time in relation to the amount of calomel formed (18° c.). (The shaded area represents $\Delta(HgCl) = \int_{t_1}^{t_2} \frac{d(HgCl)}{dt} dt$ for any given time interval ($t_1 \rightarrow t_2$).)

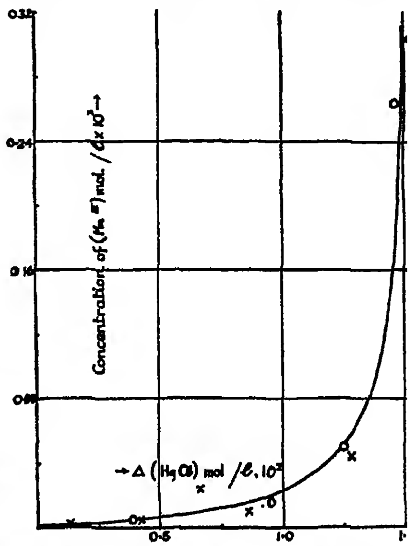

FIG. 5.—Relation between the amount of calomel formed and the concentration of (Mn^{III}) in the solution at the time of the addition of $HgCl_2$. (18° c. nitrogen atmosphere.)

—which in the brown solution is an Mn^{III} salt (or a hydrolysis product of it)—can be determined directly by adding KI, acidifying and titrating with thiosulphate.

To two identical solutions of oxalic acid (3·57 . 10^{-2} mol./l.) containing permanganate (1·43 . 10^{-3} equiv./l.), $HgCl_2$ was added (corresponding to 2·57 . 10^{-2} mol./l.) at different times : (room temperature (18° c.), nitrogen atmosphere).

(i) After 90 min. when the amount of Mn^{III} had fallen to 0·7 . 10^{-3} mol./l.

(ii) After 120 min. when the amount of Mn^{III} had fallen to 0·3 . 10^{-3} mol./l. (Here the formation of calomel started immediately after the addition of the $HgCl_2$ solution.)

After 3 hr., when the reactions had gone to completion, the amounts of calomel in the two solutions were found to be almost identical (1·52 . 10^{-3} mol./l. and 1·54 . 10^{-3} mol./l. of HgCl).

While it is thus obvious that from the point of view of chain breaking the (Mn^{3+}) in the solution should be as low as possible, it is clear that in the complete absence of Mn^{3+}, $C_2O_4^-$ is no longer produced according to the reaction :

$$Mn^{3+} + C_2O_4^{2-} = C_2O_4^- + Mn^{2+} \quad . \quad . \quad . \quad (21)$$

which normally initiates the chains.

This is shown by the Fig. 4 and 5 where the amount of Mn^{III} in the solution —at the time of the addition of $HgCl_2$ to the solution—is related to the amounts of calomel formed.

One may conclude, therefore, that the " active " oxalic acid is due to the formation of the radical $C_2O_4^-$, which has the short life of an " ordinary " radical. It is, however, produced continually over a considerable period of time by reaction (21), which will go on as long as there are Mn^{3+} ions present in the solution. Thus the seemingly long-lived " active " oxalic acid is really the Mn^{III} complex which can persist in solution for a considerable time (many hours) either as oxalic acid complex or as a hydrolysis product yielding Mn^{3+} according to the equilibria : [12, 13, 14, 14a]

$$Mn(OH)^{2+} \rightleftharpoons Mn^{3+} + OH^- \quad . \quad . \quad . \quad (22a)$$
$$Mn(C_2O_4)^+ \rightleftharpoons Mn^{3+} + C_2O_4^{2-} \quad . \quad . \quad . \quad (22b)$$
$$Mn(C_2O_4)_3^{3-} \rightleftharpoons Mn^{3+} + 3C_2O_4^{2-}. \quad . \quad . \quad . \quad (22c)$$

It has been found by Skrabal that the Mn^{III} complex is decomposed by H^+. Thus, increase of the (H^+) of the solution will lead to an accelerated decay of the activity which is in agreement with experiment.

The influence of the Mn^{3+} concentration in the solution is clearly demonstrated if the reaction is carried out in the presence of fluoride ions which form a stable complex with Mn^{3+} according to the equilibrium : [15]

$$Mn^{3+} + 4F^- \rightleftharpoons MnF_4^- \quad . \quad . \quad . \quad . \quad (23)$$

thus reducing the concentration of these ions to a low level.

This should result in :

(i) a decreased rate of production of calomel by decreasing the rate of formation of $C_2O_4^-$ (according to eqn. (21)) ;

(ii) an increase of the total chain length by inhibiting the chain-breaking processes, e.g. reaction (20) and thus leading to an increase of the total quantity of calomel formed (if only the reaction is allowed to proceed a sufficiently long time, which is necessary as the " activity " is at a very much lower level but persists for a very much longer time).

A solution containing initial concentrations of $(H_2C_2O_4)_0 = 3{\cdot}50 \,.\, 10^{-2}$ mol./l., $(KMnO_4)_0 = 1{\cdot}40 \,.\, 10^{-2}$ equiv./l., $(HgCl_2)_0 = 2{\cdot}0 \,.\, 10^{-2}$ mol./l. was allowed to react at room temperature (18° c.) in air. Under these conditions the reaction goes to completion in about 3 hr. and yields $6{\cdot}57 \,.\, 10^{-3}$ mol. HgCl/l. (expt. (1)). In a similar expt. (2), potassium fluoride was added to the solution corresponding to $(F^-) = 0{\cdot}246$ mol./l. After 3 hr. this solution only produced $2{\cdot}18 \,.\, 10^{-3}$ mol. HgCl/l., i.e. approximately one-third of the amount of expt. (1). If, on the other hand, in a similar expt. (3) with F^- ions the reaction was allowed to go to completion—which took about 36 hr.—$18{\cdot}7 \,.\, 10^{-3}$ mol. HgCl/l. were produced, nearly three times the amount of experiment (1). Another experiment carried out in nitrogen yielded $10{\cdot}7 \,.\, 10^{-3}$ mol. HgCl/l. (in 3 hr.) while in the presence of fluoride (0·246 mol./l.), $16{\cdot}7 \,.\, 10^{-3}$ mol. HgCl/l. were produced in 24 hr.

Again it is to be expected that oxidising as well as reducing agents can inhibit the formation of calomel. Molecular oxygen does in fact exert a strong inhibiting effect [2, 3] for the reasons discussed in Part I. Certain dyes such as thionine, phenosafranine, inhibit also, even at relatively low concentrations.[6] It is very likely that their strong inhibiting effect is due to their ability of undergoing oxidation and reduction reaction, and thus they may act as inhibitors both ways.

The reactions can be described in the following way (D . . . dye :

$$D + C_2O_4^- = 2CO_2 + D^- \quad . \quad . \quad . \quad (24)$$
$$(D^- + H^+ \rightleftharpoons DH \text{ (semiquinone)})$$

[14] Kehrmann, *Ber.*, 1887, 20, 1595.
[14a] cp. Taube, *J. Amer. Chem. Soc.*, 1947, 69, 1418.
[15] Cf. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (London, 1932), p. 345.
[16a] Weiss, *Nature*, 1934, 133, 648.
[16b] Weiss, *Naturwiss*, 1935, 23, 64.

followed by the formation of the leuco-dye) DH_2) :

$$2DH \rightleftharpoons D + DH_2 \quad . \quad . \quad . \quad . \quad (25)$$

which can be reoxidised again by the Mn^{3+} according to :[16]

$$(DH_2 \rightleftharpoons DH^- + H^+)$$
$$DH^- + Mn^{3+} = DH + Mn^{2+}. \quad . \quad . \quad . \quad (26)$$

In view of the extremely low stationary concentration of the $C_2O_4^-$ in the solution and the reoxidation of the leuco-dye by Mn^{3+}, it is not to be expected that the stationary concentration of the reduced dye in the solution reaches a level where it can be detected by ordinary light-absorption measurements.[6]

If reducing agents (e.g. hydroquinone) are added directly they also show an inhibiting effect.[6, 6a] This can be attributed to their interaction with the Mn^{3+} (similar to reaction (26)).

Summary.

Oxalic acid in solution if treated with an insufficient amount of an oxidising agent acquires an enhanced reactivity which manifests itself, e.g. in the reduction of mercuric chloride to calomel.

This reaction has been re-investigated particularly with regard to OH radicals as oxidising agents (as generated by the system H_2O_2-Fe^{II}).

Some evidence is presented to show that the activation of oxalic acid is due to the formation of the radical $C_2O_4^-$ which is a strong reducing agent as it easily gives off an electron with the subsequent formation of CO_2.

In the H_2O_2-Fe^{II} system the reaction and the activity ceases when all the ferrous salt is transformed to the ferric stage. The " activity " of long duration observed in the reaction with permanganate is due to the presence of Mn^{3+} ions in the solution in very low concentrations, which are stabilised by complex formation, and are capable of producing $C_2O_4^-$-radicals. This has been demonstrated by investigating the reaction in the presence of fluoride ions which are known to form a very stable complex with the Mn^{3+} ions.

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SOME EXPERIMENTS ON THE REACTIONS OF POTASSIUM SUPEROXIDE IN AQUEOUS SOLUTIONS.

By Philip George.

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The $HO^\bullet$ and $HO_2^\bullet$ radicals play an important role in the oxidation of water, in the reduction of oxygen and in the decomposition of hydrogen peroxide. Our knowledge of the reactions of the $HO^\bullet$ radical in aqueous solutions has been greatly extended by the recent investigations of Baxendale, Evans and Park.[1] Liberated by the action of Fe^{2+} ions in acidified hydrogen peroxide, competition for the $HO^\bullet$ radicals between remaining Fe^{2+} ions and polymerisable olefins added to the solution can readily be followed. The behaviour of the $HO_2^\bullet$ radical is known with far less certainty.

Potassium, rubidium and caesium superoxides, salts of the $HO_2^\bullet$

[1] Baxendale, Evans and Park, *Trans. Faraday Soc.*, 1946, 42, 155.

radical, are stable solids prepared by burning the alkali metal in oxygen.[2] KO_2 is quite stable in concentrated alkalis at low temperatures [3] but in dilute alkalis, water and dilute acids at room temperature it reacts rapidly evolving oxygen according to reaction (1) : [4]

$$2KO_2 + 2H_2O \longrightarrow O_2 + H_2O_2 + 2KOH. \quad (1)$$

This suggested that further experiments with KO_2 might furnish more information about the reactions of the $HO_2^{\bullet}$ radical. In the presence of an oxidising or reducing agent more or less oxygen might be evolved as a result of the electron-transfer reactions :

$$KO_2 + X \longrightarrow O_2 + K^+ + X^- \quad (2)$$
$$KO_2 + Y + H_2O \longrightarrow O_2H^- + KOH + Y^+ \quad (3)$$

where X and Y are the oxidising and reducing agents respectively.

Thus when KO_2 is put into water containing an oxidising or reducing agent, competition will occur between reaction (1) and reaction (2) or (3) in which a measure of the O_2 evolved will reveal the fate of the O_2^- radical. The results of a series of such experiments are given in this paper.

Experimental.

A sample of KO_2 had been prepared in 1942 by burning potassium in oxygen as described by Neumann.[5] It was kept in a sealed tube and recent analysis showed it to contain 61 % KO_2, 32·5 % K_2O_2 and 6·5 % K_2O. The O_2-evolution figures reported below give 61 % KO_2 from the reaction in water and by difference 32·5 % K_2O_2 from the reaction with strong catalase which decomposes the hydrogen peroxide formed in the KO_2 reaction and in the hydrolysis of the K_2O_2. This value for the K_2O_2 content was checked by a separate experiment in which the total H_2O_2 formed in water was titrated iodometrically with 0·1 N. $Na_2S_2O_3$. 55·1 mg. of the KO_2 sample required 8·0 ml. 0·1 N. thiosulphate, i.e. 0·145 ml. per mg. sample. This figure agrees precisely with the gasometric analysis. The remaining 6·5 % of inactive material in the sample could only be K_2O. This was confirmed by gravimetric estimation of the potassium content as sulphate and the results agree to within less than 1 % as shown in Table I. An additional check of the KO_2 content was given by a determination of the paramagnetic susceptibility of the sample with a simple Gouy balance :

TABLE I.—COMPOSITION OF KO_2 SAMPLE.

Composition.	Calculated K_2SO_4 formed (g. K_2SO_4 per g. % Oxide).
61 % KO_2	0·748
32·5 % K_2O_2	0·514
6·5 % K_2O	0·120
Total	1·38
	(1·39 from experimental determination)

$$K = 14{\cdot}8 \times 10^{-6}, \ \chi = 14{\cdot}5 \times 10^{-6}.$$

Neumann's value of χ for a pure specimen of KO_2 is $24{\cdot}2 \times 10^{-6}$, which gives a figure of 60 % KO_2 for the sample in good agreement with the oxygen evolution and gravimetric analysis data.

As far as possible Analar reagents were used in the investigation. The catalase was a specimen prepared from horse liver by the method described by Keilin and Hartree.[6]

The O_2 evolution from the KO_2 in aqueous solution was measured in two types of apparatus. In the stoichiometric determinations a 5 ml. gas burette was used connected to a special 50 ml. flask with a hollow stopper joined on in which 5-35 mg. of the sample were placed. After temperature equilibration in a thermostat,

[2] Machu, *Das Wasserstoffperoxyd und die Perverbindungen* (Julius Springer, Wein, 1937), Chap. 19.
[3] Weiss, *Trans. Faraday Soc.*, 1935, **31**, 668.
[4] Harcourt, *J. Chem. Soc.*, 1862, **14**, 267.
[5] Neumann, *J. Chem. Physics*, 1934, **2**, 31.
[6] Keilin and Hartree, *Biochem. J.*, 1945, **39**, 148.

pressure equilibration inside the stopper was made by removing a cap from a thin capillary-tube side-arm sealed on the barrel of the stopper. Turning the stopper into the flask then allowed the sample to react with 5·0 ml. of the aqueous solution chosen.

In the rate determinations the sample was placed in a small open cup resting on the bottom of a 50 ml. flask containing 4·0 ml. of the solution. Rapid shaking upset the cup and the sample reacted. The O_2 evolved was measured on a pressure gauge consisting in principle of a brass diaphragm the movement of which was magnified by a simple optical system. Calibration showed that the deflection was directly proportional to the pressure over 120 scale divisions.

$$1 \text{ div.} \equiv 0{\cdot}336 \text{ mm. paraffin (sp. gr. } 0{\cdot}788) \equiv 9{\cdot}2\ \mu\text{l. } O_2.$$

The response of the gauge to changes in pressure was practically instantaneous (much less than 1/10 sec.).

Stoichiometric Measurements.—Table II gives the volume of oxygen evolved when solid KO_2 reacts with dilute acids and alkalis, and aqueous solutions of hydrogen peroxide, ferrous and ferric sulphate, catalase and a selection of oxidising and reducing agents. The reaction flask in all runs except No. 24 was thermostated at 20° C. In run No. 24 the reaction flask was kept at 0° C.: the ozone content determined iodometrically was 0·1 ml. ozone per ml. solution. In the table the weight of the KO_2 sample in mg., the volume of oxygen corrected to N.T.P. in ml., and the ratio of ml. O_2 evolved at N.T.P. per mg. KO_2 sample are recorded.

The average values of this ratio in the reaction of the KO_2 sample with water, ferrous sulphate, ferric sulphate and catalase are:

(i) water (+ H_2SO_4, NaOH and phosphate buffer), i.e. runs 1, 2, 5, 8, 12, 21*a* and 22*a* . . . . 0·096
(ii) ferrous sulphate solution, i.e. runs 9-11 . . . . 0·126
(iii) ferric sulphate solution, i.e. runs 13-16 . . . . 0·156
(iv) strong catalase solution, i.e. runs 17-23 . . . . 0·177

Composition of the KO_2 Sample.—The decomposition of pure KO_2 in water is given by reaction (1).

$$2KO_2 + 2H_2O \longrightarrow O_2 + H_2O_2 + 2KOH \quad . \quad . \quad . \quad (1)$$

This enables the percentage KO_2 in the sample used in the above measurements to be calculated. Pure KO_2 liberates 0·158 ml. O_2 per mg. at N.T.P. The sample evolved 0·096 ml. O_2 at N.T.P. and thus contains 61 °/₀ KO_2. If a catalyst that decomposes H_2O_2 is added to the aqueous solution after reaction (1) is completed, a further amount of oxygen is liberated equivalent to half that in reaction (1).

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad . \quad . \quad . \quad . \quad (4)$$

Alternatively, if the KO_2 is added to an aqueous solution of the catalyst all the available oxygen is evolved. This has been done in runs 21*a* and 22*a* and runs 17-22 respectively (Table II) using the enzyme catalase. 0·081 ml. O_2 per mg. sample is liberated from the hydrogen peroxide. From the peroxide formed in the KO_2 decomposition 0·096/2 ml. O_2 per mg. is evolved, i.e. 0·048, thus leaving 0·033 ml. O_2 unaccounted for. The most likely source of this is some K_2O_2 in the KO_2 sample: the figure corresponds to 32·5 °/₀: this was checked by iodometric titration of the peroxide liberated by hydrolysis. Thus these data give the composition of the samples 61 °/₀ KO_2 and 32·5 °/₀ K_2O_2. Gravimetric analysis of the potassium content confirmed the remaining 6·5 °/₀ as K_2O.

Rate Measurements.—The rate of oxygen evolution as the KO_2 sample decomposes in water and aqueous solutions of ferrous sulphate, ferric sulphate and catalase has been measured. This is the minimum rate and not the real rate since the reaction is between a solid and liquid.

In the stoichiometric measurements the KO_2 sample, during equilibration, was kept in a dry atmosphere in the hollow stopper. In the rate measurements, carried out with identical solutions at the same temperature, the reaction flask containing the solution was allowed to attain the temperature of the thermostat before the KO_2 sample in the open tube was placed on the bottom of the flask. A further 2-3 min. was then required before final temperature equilibrium was reached. In this time a little KO_2 reacted with the moist air inside the flask and so the oxygen evolution from a given solution was less than that recorded in the stoichiometric determinations. For this reason the results of the rate measurements are presented in the following way. From the total oxygen

evolved in the rate measurement the actual amount of the KO_2 sample present at the beginning of the reaction was calculated from the average values for oxygen evolved obtained in the stoichiometric determinations in Table II. Using these calculated amounts the ratio ml. O_2 per mg. KO_2 sample was calculated for the observed values of the oxygen evolved at 2, 5, 10, 15, 20, 25 and 30 sec. from the beginning of the reaction. For example, a sample of KO_2 reacting with 1·0 M. phosphate buffer pH 5·8 evolved these quantities of oxygen at the above time intervals: 0·275, 0·301, 0·327, 0·327, 0·335, 0·335, 0·335 ml. The average value

TABLE II.

OXYGEN EVOLVED FROM THE KO_2 SAMPLE IN VARIOUS AQUEOUS SOLUTIONS.

Run Number.	Solution.	Mg. KO_2 Sample.	Ml. O_2 at N.T.P.	Ml. O_2 per mg. KO_2 Sample.
1	0·1 N. H_2SO_4	9·9	1·08	0·109
2	0·1 N. NaOH	17·3	1·85	0·107
3	80 vol. H_2O_2 in 0·1 N. H_2SO_4	28·6	2·74	0·096
4	80 vol. H_2O_2 in 0·1 N. H_2SO_4	33·4	3·57	0·107
5	0·1 N. NaOH	22·8	1·96	0·086
6	80 vol. H_2O_2 in 0·1 N. NaOH	30·0	3·03	0·101
7	80 vol. H_2O_2 in 0·1 N. NaOH	17·0	1·45	0·086
8	0·1 N. H_2SO_4	24·4	2·11	0·087
9	1·0 M. $FeSO_4$ in 4·0 N. H_2SO_4	17·5	2·20	0·126
10	1·0 M. $FeSO_4$ in 4·0 N. H_2SO_4	15·6	1·87	0·120
11	1·0 M. $FeSO_4$ in 0·1 N. H_2SO_4	18·0	2·39	0·132
12	0·1 N. H_2SO_4	19·2	1·73	0·090
13	1·0 M. $Fe_2(SO_4)_3$	22·4	3·56	0·158
14	1·0 M. $Fe_2(SO_4)_3$ in 4·0 N. H_2SO_4	18·6	2·72	0·146
15	1·0 M. $Fe_2(SO_4)_3$	20·2	3·15	0·156
16	0·3 M. [$Fe_2(SO_4)_3$ + $Fe(OH)_3$ sol.]	22·7	3·68	0·162
17	Strong catalase in 1·0 M. phosphate buffer, pH 5·8	12·5	2·37	0·189
18	Strong catalase in 1·0 M. phosphate buffer, pH 5·8	8·4	1·45	0·173
19	Strong catalase in 1·0 M. phosphate buffer, pH 5·8	8·7	1·37	0·159
20	Strong catalase in 1·0 M. phosphate buffer, pH 5·8	13·6	2·54	0·187
21*a*	1·0 M. phosphate buffer pH 5·8, then	17·3	1·66	0·096
21*b*	Strong catalase	17·3	1·46	0·085
22*a*	1·0 M. phosphate buffer pH 5·8, then	20·9	1·87	0·089
22*b*	Strong catalase	20·9	1·49	0·072
23	Strong catalase in 1·0 M. phosphate buffer pH 5·8	23·2	3·96	0·171
24	Neutral sat. Br_2 water	7·9	1·40	0·179
25	0·1 °/$_o$ Gold Chloride in 2·0 M. HCl	9·3	1·33	0·155
26	Neutral solution of ozone	11·7	1·03	0·088
27	Sat. soln. $(NH_4)_2S_2O_8$ in 0·1 N. H_2SO_4	16·6	2·05	0·124
28	Sat. soln. $Na_2S_2O_8$ in 0·1 N. NaOH	5·7	0·97	0·171
29	Sat. soln. $Na_2S_2O_8$ in 0·1 M. $AgNO_3$	19·0	3·36	0·177
30	Sat. soln. $SnCl_2$ in 2·0 M. HCl	6·05	0·61	0·100
31	1·0 M. $Na_2S_2O_4$ in 0·1 N. NaOH	16·3	1·52	0·093

of oxygen evolved per mg. is 0·096 ml. from Table II: therefore 3·5 mg. of KO_2 sample reacted and the oxygen evolution figures now expressed as ml. per mg. sample are 0·079, 0·086, 0·094, 0·094, 0·096, 0·096, and 0·096. The mean results of several determinations are given in Fig. 1 for the following solutions: curve *a*, 1·0 M. phosphate buffer, pH 5·8; curve *b*, 0·1 N. H_2SO_4; curve *c*, strong catalase in 1·0 M. phosphate buffer, pH 5·8.

In Fig. 2 *a*, *b* and *c*, oxygen evolution curves are given for identical ferric sulphate, ferrous sulphate and catalase solutions reacting with 0·05 ml. 8·6 vol. H_2O_2 in the open tube instead of the KO_2 sample. The marked difference between the curves in Fig. 1 and 2 will be discussed later.

The small peak in curves 1*b*, *c* and *d* and 2*b* is in all probability a thermal effect, the oxygen being evolved so rapidly that it carries away some of the heat of reaction and a few sec. elapse before temperature equilibrium in the gas phase is reached again.

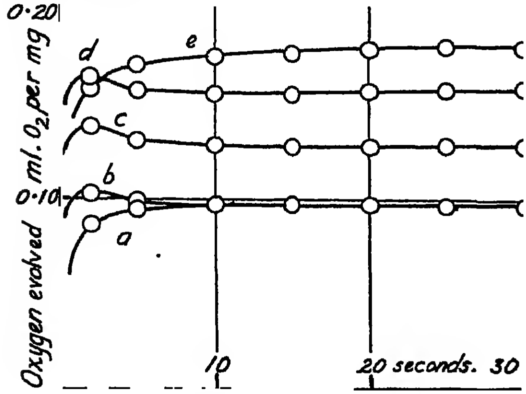


FIG. 1.—Oxygen evolved from the KO_2 sample in various aqueous solutions plotted against time.

Curve *a*: 1·0 M. phosphate buffer *p*H 5·8.
Curve *b*: 0·1 N. H_2SO_4.
Curve *c*: 1·0 M. $FeSO_4$ in 0·1 N—H_2SO_4.
Curve *d*: 1·0 M. $Fe_2(SO_4)_3$.
Curve *e*: strong catalase in 1·0 M. phosphate buffer, *p*H 5·8.

Summary of Experimental Results.

The stoichiometric measurements given in Table II show that in all cases the oxygen evolution reaction (1) completely predominates. With the sample of KO_2 used this reaction yields 0·096 ml. O_2 per mg. If the H_2O_2 formed from the KO_2 and in the hydrolysis of the K_2O_2 is also decomposed as in reaction (4) then a total of 0·177 ml. O_2 per mg. is evolved. Table II shows that in no case is the oxygen evolved on the average less than 0·096 or greater than 0·177 ml. O_2 per mg. These experiments thus show that under the given conditions reactions (1) and (4) are most important and that with oxidising and reducing agents the direct oxidation of O_2^- giving O_2 gas and the direct reduction of O_2^- giving $O_2^{=}$ (i.e. H_2O_2) are insignificant. The rate measurements show that reaction (1) is extremely fast; all the oxygen is evolved in about 2 sec. The peroxide decomposition reaction (4) with ferrous ions, ferric ions and catalase is also very rapid. This will be discussed later.

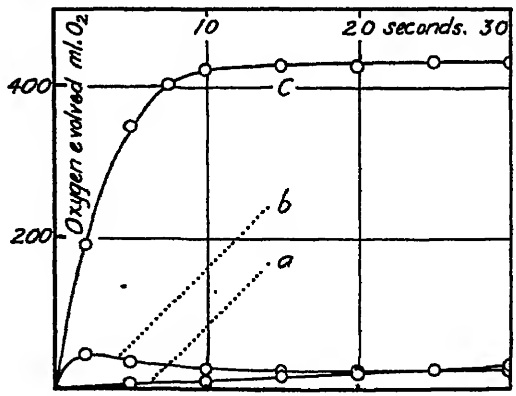


FIG. 2.—Oxygen evolved from 0·05 ml. 8·6 vol. H_2O_2 in various aqueous solutions plotted against time.

Curve *a*: 1·0 M. $Fe_2(SO_4)_3$.
Curve *b*: 1·0 M. $FeSO_4$ in 0·1 N. H_2SO_4.
Curve *c*: strong catalase in 1·0 M. phosphate buffer, *p*H 5·8.

Discussion.

The stability of O_2^-, the anion of the $HO_2^{\bullet}$ radical, in solid KO_2 at room temperature is in part due to the slow electron transfer between two O_2^- anions in the crystal lattice:

$$2O_2^- \longrightarrow O_2 + O_2^{=}.$$

At high temperatures, for instance in the oxidation of molten potassium, this reaction does become important and whilst KO_2 is formed initially an equilibrium mixture containing about 67 % KO_2 and 33 % K_2O_2 results on prolonged heating.[4] KO_2 may also be prepared by passing ozone into cold conc. KOH[5]. The stability of the O_2^- anion in this solution makes clear the sequence of reactions responsible for the oxygen evolution in water.

Proton and Electron Transfer in the Evolution of Oxygen from KO_2.—The evolution of oxygen from solid KO_2 in dilute alkalies, water and dilute acids is given by reactions (1*a*) and (1*b*) where the symbol $[O_2^- . O_2^-]$ represents two O_2^- anions in the solid KO_2.

$$[O_2^- . O_2^-] + H_2O \longrightarrow O_2 + O_2H^- + OH^- \quad . \quad (1a)$$
$$[O_2^- . O_2^-] + H_3O^+ \longrightarrow O_2 + O_2H^- + H_2O. \quad . \quad (1b)$$

The stability of KO_2 in concentrated alkalies, where no proton transfer is possible according to reaction (1*c*),

$$[O_2^- . O_2^-] + OH^- \longrightarrow O_2 + HO_2^- + O^= \quad . \quad . \quad (1c)$$

shows that reactions (1*a*) and (1*b*) are composite. First, proton transfer must occur giving the HO_2 radical as in (1*d*) or (1*e*), then electron transfer between O_2^- and $HO_2^{\bullet}$ completes the reaction and oxygen is evolved (1*f*).

$$[O_2^- . O_2^-] + H_2O \longrightarrow [O_2^- . O_2H^{\bullet}] + OH^- \quad . \quad . \quad (1d)$$
$$[O_2^- . O_2^-] + H_3O^+ \longrightarrow [O_2^- . O_2H^{\bullet}] + H_2O \quad . \quad . \quad (1e)$$
$$[O_2^- . O_2H^{\bullet}] \longrightarrow O_2\,(gas) + O_2H^-. \quad . \quad . \quad (1f)$$

Reactions (1*d*) and (1*e*) result from the collision of H_2O or H_3O^+ molecules with the particle of KO_2 and are fairly certainly the rate-determining steps for the final electron-transfer reaction (1*f*) needs no ordinary collision since the intermolecular distance $O_2^- \ldots O_2H^{\bullet}$ will still be approximately that of $O_2^- \ldots O_2^-$ in the KO_2 crystal lattice. The entire reaction resembles very closely an electrode reaction, a proton passes to the surface of the KO_2 and its charge is taken up by electron migration between O_2^- anions. The rate measurements given above support this interpretation for in acid solution the oxygen is evolved more rapidly (Fig. 1*a* and *b*).

Competition between Proton and Electron Transfer in the Reactions of KO_2.—This mechanism established for the oxygen evolution shows that when KO_2 is put into water containing an oxidising or reducing agent the competition that occurs is between the proton-transfer reactions (1*c*) and (1*d*) and electron-transfer reactions (2*a*) and (3*a*), where X and Y are the oxidising and reducing agents.

$$O_2^- + X \longrightarrow O_2 + X^- \quad . \quad . \quad . \quad . \quad (2a)$$
$$O_2^- + H_2O + Y \longrightarrow O_2H^- + OH^- + Y^+ \quad . \quad (3a)$$

The stoichiometric measurements given in Table II show that in all cases the proton transfer predominates and no electron transfer could be detected with hydrogen peroxide, ferrous and ferric salts, catalase, bromine water, gold chloride, ozone, persulphate ions, stannous chloride or sodium hydrosulphite. With the non-metallic reducing agents oxygen was still evolved as in reaction (1). With oxidising agents and with metallic ions, both electron acceptors and donors, additional oxygen was evolved which could be accounted for simply by partial or complete decomposition of the hydrogen peroxide formed from the KO_2 and from the hydrolysis of the K_2O_2. Since the concentration of the water, about 50 M., is so much greater than that of the oxidising-reducing agents and surrounded as they are by hydration shells, the proton-transfer reaction is considerably favoured. Nevertheless it is interesting that such powerful reagents as persulphate and hydrosulphite ions have no perceptible effect.

Two reactions in particular might have yielded a greater quantity of

oxygen as in reaction (2a): these are with ozone and with bromine where in their reactions with hydrogen peroxide Taube and Bray [7] and Callow, Griffiths and McKeown [8] have presented kinetic evidence which suggests that the reactions with the $HO_2^\bullet$ radical are very fast chain-propagating steps.

$$O_3 + HO_2^\bullet \longrightarrow 2O_2 + OH^\bullet$$
$$Br_2 + HO_2^\bullet(O_2^-) \longrightarrow O_2 + HBr(Br^-) + Br^\bullet.$$

In the case of ozone the reason why the reaction is not observed is very probably that as soon as any $HO_2^\bullet$ radical is formed it reacts with an adjacent O_2^- in the lattice according to reaction (1f). There is no possibility here of a direct reaction between O_3 and O_2^- for O_2^- can be prepared by passing O_3 into cold concentrated KOH[3]. A direct reaction could occur though between Br_2 and O_2^- but in this case the proton-transfer reactions are apparently faster.

The kinetics of the reaction between hydrogen peroxide and ozone, and the photo-reaction between hydrogen peroxide and bromine suggest that the direct reaction between O_2^- or $HO_2^\bullet$ and H_2O_2 is insignificant in the bulk of the solution. The consumption ratios

$$\frac{H_2O_2 \text{ decomposed}}{O_3 \text{ decomposed}} \text{ and } \frac{H_2O_2 \text{ decomposed}}{Br_2 \text{ decomposed}}.$$

were both found to be unity.[7, 8] This reaction between O_2^- or $HO_2^\bullet$ and H_2O_2 is one of the two proposed by Haber and Weiss [9, 10] to propagate a chain in the decomposition of hydrogen peroxide (reaction (5)).

$$H_2O_2 + HO_2^\bullet\,(O_2^-) \longrightarrow H_2O(OH^-) + O_2 + OH^\bullet. \quad . \quad (5)$$

Bray [11] pointed out that the evolution of oxygen from KO_2 in water furnishes additional evidence against this reaction for none of the H_2O_2 formed is decomposed whilst the remaining KO_2 reacts. The failure to observe any reaction between KO_2 and ozone or bromine (Table II) does not invalidate the argument for the following reason.

The H_2O_2 is formed *in situ* from the decomposition of the KO_2 and the hydrolysis of the K_2O_2 and is therefore present in high concentration to compete with the proton-transfer reactions (1d) and (1e). The speed of the proton transfer must be at least 50 times greater, for about 2 °/₀ of the reaction with hydrogen peroxide could have been detected in the stoichiometric experiments. These experiments thus confirm Bray's conclusion and strongly suggest that in the catalytic decomposition of hydrogen peroxide, oxygen is evolved not by reaction (5) but by some other mechanism.

Stoichiometry of the Reaction between KO_2 and Ferrous and Ferric Salts.—The results in Table II show no evidence of direct electron transfer between O_2^- in the KO_2 and Fe^{2+} or Fe^{3+}. In both cases oxygen is evolved from the KO_2 according to reaction (1) and in addition 37·5 °/₀ and 75 °/₀ of the hydrogen peroxide formed is decomposed catalytically according to reaction (4). This extensive decomposition of the peroxide is rather surprising. If a small quantity of H_2O_2 comparable to that formed from the KO_2 and K_2O_2 is dropped into identical ferrous or ferric salt solutions far less decomposition occurs in the same time interval, i.e. about 5 °/₀—see Fig. 2a, b and c.

There are several possible reasons for this. First, in the experiment with hydrogen peroxide, diffusion throughout the bulk of the liquid could rapidly lower its relative concentration whereas with the KO_2 sample the peroxide produced might react before diffusion occurs. Secondly, in

[7] Taube and Bray, *J. Amer. Chem. Soc.*, 1940, **62**, 3357.
[8] Callow, Griffiths and McKeown, *Trans. Faraday Soc.*, 1939, **35**, 559.
[9] Haber and Weiss, *Proc. Roy. Soc. A*, 1934, **147**, 332.
[10] Weiss, *Trans. Faraday Soc.*, 1935, **31**, 1547.
[11] Bray, *J. Amer. Chem. Soc.*, 1938, **60**, 82.

the experiments with KO_2, the peroxide is produced in a strongly alkaline environment and the concentration of O_2H^- might temporarily be much greater than the concentration of H_2O_2. Fe^{3+} reacts far faster with O_2H^- as shown in the experiments of von Bertelan [12] and Haber and Weiss.[9] Thirdly, the alkaline environment around the KO_2 particle might convert the Fe^{2+} and Fe^{3+} ions into $FeOH^+$ and $FeOH^{2+}$ with a concomitant alteration in their reactivity. Fourthly, in the decomposition of the peroxide from the $KO_2^{\bullet}$ radicals might be formed which could react rapidly with any KO_2 left.

It is certain that diffusion and the alkaline environment around the KO_2 particle play a part for otherwise all the available peroxide would be decomposed by ferric ions rather than the 75 % observed. An experiment to check this was planned using sodium peroxide in place of the KO_2 sample, to yield only O_2H^-, then H_2O_2, by hydrolysis. However, a small but very rapid oxygen evolution from the sodium peroxide in dilute acids and alkalies indicated some 10 % of the higher oxide NaO_2 in the specimen. This surprising result has been confirmed * and the experiments with Fe^{3+} and Fe^{2+} ions and pure Na_2O_2 will be reported in a later paper.

Rate of Oxygen Evolution in the Reaction between KO_2 and Ferrous Sulphate, Ferric Sulphate and Catalase.—Fig. 1, curves *b*, *c* and *d*, show that all the oxygen produced in the reaction of the KO_2 sample in acidified water, acidified ferrous sulphate and ferric sulphate is liberated within 2 sec. from the beginning of the reaction. These results are very significant and have been replotted in Fig. 3. Curve *a* gives the oxygen evolution from KO_2 in 0·1 N. H_2S_4O, curves *b* and *c* the oxygen evolution from the H_2O_2 produced in the decomposition of the KO_2 and the hydrolysis of the K_2O_2 by the ferrous and ferric salts respectively. Their significance lies in the fact that under experimental conditions where no sign of a direct reaction between O_2^- and H_2O_2 can be detected, oxygen is evolved extremely rapidly in a catalytic decomposition of hydrogen peroxide. The experiments even suggest that the speed of this catalytic decomposition is comparable to that of the KO_2 reacting with water.

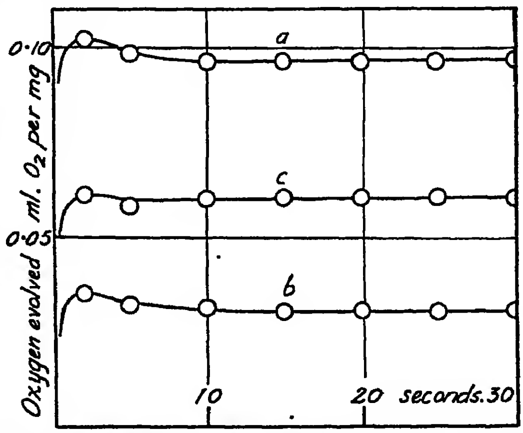


FIG. 3.—Separate curves showing the oxygen evolved from KO_2 and from the hydrogen peroxide formed from KO_2 and K_2O_2, plotted against time.

Curve *a*: KO_2 sample in 0·1 N. H_2SO_4 (identical to 1*b*).
Curve *b*: 1·0 M. $FeSO_4$ in 0·1 N. H_2SO_4 reacting with the H_2O_2 formed *in situ* (obtained by subtracting 1*b* from 1*c*).
Curve *c*: 1·0 M. $Fe_2(SO_4)_3$ reacting with the H_2O_2 formed *in situ* (obtained by subtracting 1*b* from 1*d*).

[12] Von Bertelan, *Z. physik. Chem.*, 1920, **95**, 328.

* SODIUM PEROXIDE: The two samples examined were pale yellow in colour and in water rapidly evolved a small quantity of oxygen corresponding to about 10 % of the higher oxide NaO_2. The samples were paramagnetic $\chi = 2{\cdot}65$ and $2{\cdot}17 \times 10^{-6}$ corresponding to 11 % and 9 % of NaO_2 present. Determinations of the sodium content confirmed this. Thus, although not yet isolated in the pure state, the highest oxide of sodium appears to be NaO_2 and not Na_2O_2 as usually accepted.[2] A full account of this will be published shortly.

The following conclusions can therefore be drawn. First that under these experimental conditions the chain-propagation reaction, proposed by Haber and Weiss [9, 10] for the evolution of oxygen in the catalytic decomposition of hydrogen peroxide, does not occur (reaction (5)). Secondly, in the place of this reaction there is another mechanism for oxygen evolution. This other mechanism may be some variant of the KO_2 reaction (1) such as the mutual reaction of HO_2 radicals, or a reaction of O_2^- or $HO_2^{\bullet}$ with Fe^{3+}, although this seems unlikely since no evidence for it could be detected in the reaction of the KO_2 sample with ferric salts.

It must be emphasised that in the first instance these conclusions refer only to the decomposition of hydrogen peroxide formed *in situ* from KO_2 and K_2O_2. Relative concentrations of reactants and the acidity of the medium are very different in the reaction of ferrous and ferric salts and hydrogen peroxide in homogeneous solution. Nevertheless the existence of this rapid reaction evolving oxygen must be taken into account especially if there is no kinetic evidence for a chain mechanism as in the ferric ion-catalysed decomposition.[9, 11]

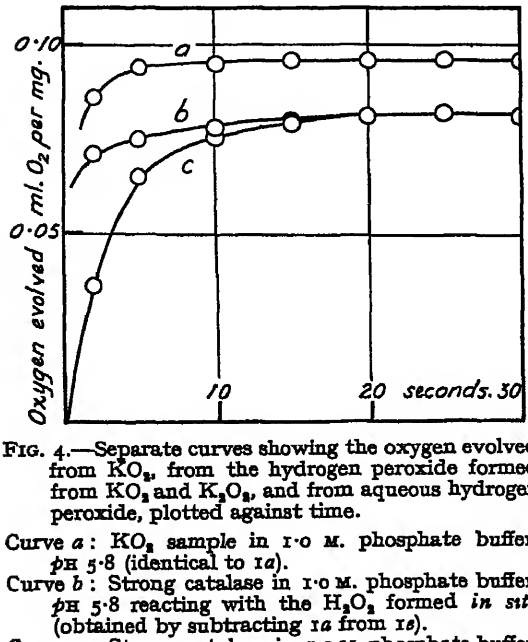


FIG. 4.—Separate curves showing the oxygen evolved from KO_2, from the hydrogen peroxide formed from KO_2 and K_2O_2, and from aqueous hydrogen peroxide, plotted against time.

Curve *a*: KO_2 sample in 1·0 M. phosphate buffer, pH 5·8 (identical to 1*a*).
Curve *b*: Strong catalase in 1·0 M. phosphate buffer, pH 5·8 reacting with the H_2O_2 formed *in situ* (obtained by subtracting 1*a* from 1*e*).
Curve *c*: Strong catalase in 1·0 M. phosphate buffer, pH 5·8 + 0·05 ml. 8·6 vol. H_2O_2 (2*c* redrawn to scale of 4*b*).

Similar conclusions can be drawn from the experiments in which catalase was used. Fig. 1, curves *a* and *e*, show that in the reaction of the KO_2 sample with phosphate buffer pH 5·8 and with strong catalase in the same buffer solution 90 % of the total oxygen is evolved in the first 2 sec., and the evolution is complete in about 5 sec. The results are replotted in Fig. 4; curve *a* gives the evolution of oxygen from the KO_2 sample in the buffer solution, curve *b* the evolution from the H_2O_2 produced from the KO_2 and K_2O_2, and curve *c* gives the evolution from aqueous H_2O_2 itself redrawn to the scale of curve 4*b* from the points of Fig. 2, curve *c*.

By a similar argument to that above it follows that catalase evolves oxygen from the peroxide formed *in situ* by some mechanism other than the direct reaction of O_2^- or $HO_2^{\bullet}$ with H_2O_2. Yet, whilst in the reactions of ferrous and ferric ions no direct conclusion could be reached on the decomposition of the peroxide in homogeneous solution, this is possible for catalase. Curve 4*c* shows that when aqueous hydrogen peroxide is added to strong catalase the total oxygen is evolved in about 10 sec. In the same time interval and in an identical buffer solution, KO_2 reacts evolving its oxygen with no detectable reaction between O_2^- or $HO_2^{\bullet}$ and H_2O_2. This proves that in the decomposition of hydrogen peroxide by catalase the chain-propagation reaction proposed by Haber and Weiss plays no part and that the oxygen is evolved by some other mechanism.

Summary.

A sample of potassium superoxide containing 61 % KO_2, 32·5 % K_2O_2 and 6·5 % K_2O was used in gasometric experiments to study the reactions of the O_2^- free radical in aqueous solutions.

Evidence is presented which shows that in water, dilute acids and dilute alkalies, oxygen is evolved as a consequence of proton transfer (*a*) followed by rapid electron transfer (*b*).

$$2O_2^- + H_2O(H_3O^+) \longrightarrow [O_2^- . O_2H^\bullet] + OH^-(H_2O) \quad . \quad . \quad (a)$$
$$[O_2^- . O_2H^\bullet] \longrightarrow O_2 + O_2H^- \quad . \quad . \quad . \quad . \quad . \quad (b)$$

In aqueous solutions of oxidising and reducing agents these reactions completely predominate and no increase or decrease respectively in the amount of oxygen evolved attributable to direct electron transfer with O_2^- could be detected with hydrogen peroxide, ferrous and ferric salts, catalase, bromine water, gold chloride, ozone, persulphate ions, stannous chloride or sodium hydrosulphite. In some cases, with the metallic salts in particular, oxygen was evolved in addition to that from reaction (*b*) which could be accounted for simply by partial or complete decomposition of the hydrogen peroxide formed *in situ* from the KO_2 and from the hydrolysis of the K_2O_2. With ferrous salts, ferric salts and catalase 37·5 %, 75 % and 100 % decomposition of the peroxide into oxygen was observed.

This additional oxygen evolution occurred almost as rapidly as in the primary reactions (*a*) and (*b*) and under conditions where no sign of a direct reaction between O_2^- and H_2O_2 could be detected. Thus this potential chain-propagation reaction for the evolution of oxygen in the catalytic decomposition of hydrogen peroxide

$$H_2O_2 + O_2^- \longrightarrow OH^- + O_2 + OH^\bullet \quad . \quad . \quad . \quad (c)$$

does not occur with ferrous salts, ferric salts and catalase under these experimental conditions, but the oxygen is evolved by some other mechanism.

The rapid reaction of catalase with hydrogen peroxide whose concentration is comparable to that obtained in the experiments with KO_2 shows conclusively, that this oxygen evolution reaction (*c*) plays no part in the familiar decomposition of H_2O_2 by the enzyme.

Résumé.

On a employé le peroxyde de potassium pour étudier gazométriquement la réaction des radicaux libres O_2^- en solutions aqueuses. Dans l'eau, les acides et les alcalis dilués, de l'oxygène se dégage, d'après la réaction (1), suivie de (2) :

$$(1)\ 2O_2^- + H_2O(H_3O^+) \rightarrow [O_2^- . O_2H^\bullet] + OH^-(H_2O)\,;$$
$$(2)\ [O_2^- . O_2H^\bullet] \rightarrow O_2 + O_2H^-.$$

Dans des solutions d'agents réducteurs et oxydants, ces réactions dominent, mais dans quelques cas la quantité d'oxygène libérée est supérieure ; ceci s'explique par la décomposition de l'eau oxygénée formée dans le milieu à partir de KO_2 et par hydrolyse de K_2O_2.

Zusammenfassung.

Kaliumsuperoxyd ist dazu benützt worden, um auf gasometrischem Wege die Reaktionen von O_2^--Radikalen in wässerigen Lösungen zu untersuchen. In Wasser und verdünnten Säuren und Basen wird Sauerstoff auf dem Wege der aufeinanderfolgenden Reaktionen (1) und (2) gebildet

$$(1)\ 2O_2^- + H_2O(H_3O^+) \rightarrow [O_2^- . O_2H^\bullet] + OH^-(H_2O)\,;$$
$$(2)\ [O_2^- . O_2H^\bullet] \rightarrow O_2 + O_2H^-.$$

In Lösungen von oxydierenden und reduzierenden Substanzen herrschen diese Reaktionen vor, aber in manchen Fällen wird mehr Sauerstoff gebildet, was durch die Zersetzung des *in situ* aus KO_2 gebildeten Wasserstoffperoxyds und durch Hydrolyse von K_2O_2 erklärt wird.

The Molteno Institute,
University of Cambridge.

GENERAL DISCUSSION.

Prof. M. G. Evans, Dr. J. H. Baxendale and Mr. D. J. Cowling (*Leeds*) (*communicated*) : In a previous publication[1] we showed that the primary steps in the reaction between hydrogen peroxide and a reducing agent is

$$HO{-}OH + e \rightarrow HO^- + OH. \quad (1)$$

This is followed by a second electron-transfer step involving the OH radical :

$$HO + e \rightarrow HO^-. \quad (2)$$

We are able to show that the formation of OH radicals could be deduced from their action in initiating the polymerisation of vinyl compounds :

$$HO + \underset{\textstyle R}{CH_2{=}CH} \rightarrow HO.CH_2.\underset{\textstyle R}{\underset{|}{CH}}{-} \quad (3)$$

$$HOCH_2{-}\underset{\textstyle R}{CH}{-} + \underset{\textstyle R}{CH_2{=}CH} \rightarrow HOCH_2{-}\underset{\textstyle R}{\underset{|}{CH}}{-}CH_2{-}\underset{\textstyle R}{\underset{|}{CH}}{-}$$

At sufficiently high concentrations of vinyl compounds, reaction (3) had the effect of suppressing reaction (2), thus leading to a change in the stoichiometry from $[H_2O_2] \equiv 2e$ in the absence of vinyl compound to $[H_2O_2] \equiv e$ in the presence of a sufficiently high concentration of polymerisable compound. This type of study is an instructive way of investigating the conditions of formation of free radicals arising from primary electron-transfer reactions.

We have recently extended this field of investigation to include not only H_2O_2 but also compounds of the type HOX in which X is chlorine or bromine. We have chiefly used ferrous ions as our source of electrons but have also investigated the reactions with iron complexes. We wish to report here the preliminary results obtained with HOBr.

In the case of HOBr the primary reaction might be either :

$$e + HOBr \rightarrow HO^- + Br \quad (4a)$$

or

$$e + HOBr \rightarrow HO + Br^- \quad (4b)$$

An investigation of the stoichiometry not only of the iron but also of the halide ion as a function of monomer concentration will decide between these two possibilities. Thus if reaction (4*a*) is followed by

$$Br + \underset{\textstyle R}{CH_2{=}CH} \rightarrow BrCH_2{-}\underset{\textstyle R}{CH}{-}$$

then the amount of halide ion formed with increasing monomer concentration should decrease. If, however, the primary step is (4*b*) followed by

$$HO + \underset{\textstyle R}{CH_2{=}CH} \rightarrow HOCH_2{-}\underset{\textstyle R}{\underset{|}{CH}}{-}$$

then the amount of halide ion formed will be independent of the monomer concentration. The experimental results are shown in Fig. 1 and lead to the conclusion that the primary reaction is the formation of the halogen atom. We suggest that the reason for this is that the electron affinity plus the heat of solvation is greater for the OH radical than for the bromine atom, and hence the heat of reaction (4*a*) is more exothermic than that of reaction (4*b*).

[1] Baxendale, Evans and Park, *Trans. Faraday Soc.*, 1946, **42**, 155.

In Fig. 1 we show the results obtained with hydrogen peroxide under comparable conditions, and it is important to notice that the presence of a monomer is much more effective in suppressing reaction (2) in the case of OH radicals than in the case of bromine atoms. The rate which these curves fall off with monomer concentrations is related to the ratio of velocity constants k_3/k_2 for reactions

$$X + \underset{\text{R}}{CH_2{=}CH} \rightarrow XCH_2 . \underset{\text{R}}{CH}— \quad k_3$$

$$X + Fe^{++} \rightarrow X^- + Fe^{+++} \quad k_2$$

Because the carbon-bromine bond strength is weaker than the carbon—OH we can predict that the velocity constant k_3 will be less for bromine than for the hydroxyl radical. On the other hand, reaction k_2 is exothermic both for bromine atoms and hydroxyl radicals, and as yet little is known about the velocity constants of such reactions. We would suggest,

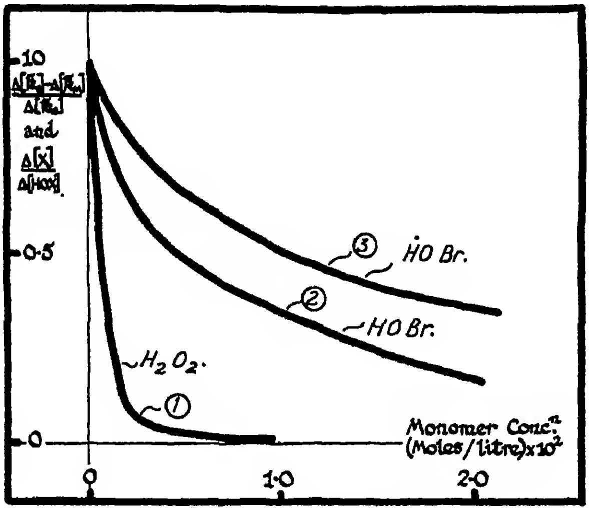


FIG. 1.—Initial concentrations.

Curve (1) H_2O_2: 8×10^{-4} M.
Fe^{++}: 16×10^{-4} M.

Curve (3) HOBr: 10×10^{-4} M.
Fe^{++}: 37×10^{-4} M.

Curve (2) HOBr: 8×10^{-4} M.
Fe^{++}: 15×10^{-4} M.

Curve (2) Refers to the change in ferrous ion and bromide ion concentration.

however, that it is the change in the velocity constant k_3 which is responsible for the greater effectiveness of monomer in the case of hydrogen peroxide as compared with its action in the case of HOBr.

Dr. J. Weiss (*Newcastle*) said: It is of interest that Dr. Waters has produced some fresh evidence for the RCHOH radicals which were first proposed by Haber and Willstätter in 1931 and which also play a very important part in the mechanism of the Cannizarro reaction.[1]

Dr. G. J. Minkoff (*London*) *said*: In view of the large number of postulated free radical mechanisms involving hydrogen peroxide, I should like to draw attention to the fact that not all the reactions of hydrogen peroxide involve such mechanisms. Dr. Bunton, Mr. Everett and I have been investigating the reactions between aldehydes and peroxides

[1] Cf. Weiss, *Trans. Faraday Soc.*, 1941, 37, 770.

in organic solutions. We have found considerable evidence in favour of an ionic mechanism of the type

$$H_2O_2 \rightleftharpoons HO_2^- + H^+,$$

$$HO_2^- + CH_3C\begin{matrix}\diagup H\\ \diagdown O\end{matrix} \rightleftharpoons CH_3C\begin{matrix}\diagup H\\ -OH\\ \diagdown OO^-\end{matrix} \overset{H^+}{\rightleftharpoons} CH_3C\begin{matrix}\diagup H\\ -OH.\\ \diagdown OOH\end{matrix}$$

For example, these reactions are insensitive to illumination by daylight, are catalysed by acids and by bases, and proceed faster in solution than in the gas phase. It is hoped that a report of these investigations will be published shortly.

Dr. M. J. S. Dewar (*Maidenhead*) said: Dr. Waters has suggested [3] that the Criegee and Malaprade reactions proceed by a free-radical mechanism analogous to the oxidations with Fenton's reagent. This seems unlikely. Firstly, the oxidations of glycols by HIO_4 or $Pb(OAc)_4$ proceed rapidly and quantitatively under conditions where the oxidants are stable; nor do the reactions show the characteristics of radical-chain reactions. Secondly, oxidation of tartaric acid with Fenton's reagent gives dioxymaleic and dioxytartaric acids; but oxidation of the acid with HIO_4 gives a quantitative yield of glyoxilic acid, and oxidation of ethyl tartrate with $Pb(OAc)_4$ gives about 90 % of ethyl glyoxilate. The mechanisms of the reactions must therefore differ. It seems more likely that the HIO_4 and $Pb(OAc)_4$ oxidations proceed by simple bimolecular reaction through transition states of the type (I)

$$\begin{matrix} R_2C\text{—}\!\cdot\!\cdot\!\cdot O\,.\,.\,H\,.\,.\,.\,AcO\diagdown \\ \qquad\qquad\qquad\qquad\qquad\quad PbO(Ac)_2 \\ R_2C\cdot\!\cdot\!\cdot\text{—}O\,.\,.\,H\,.\,.\,.\,AcO\diagup \end{matrix}$$

(I)

Dr. W. A. Waters (*Oxford*) said: The experimental study of the mechanism of glycol-splitting is a problem on which Mr. Merz and I are now engaged, and I should like to make the present factual position quite clear.

The free ·OH radical can undoubtedly bring about glycol-splitting, because the H_2O_2—Fe^{++} mixture converts pinacol to acetone quite rapidly. This, however, is *not* a chain reaction, and, since there is no reduction of Hg^{++}, it must necessarily involve the attack of O—H bonds, thus:

$$C\text{—}O\text{—}H + {}^\bullet OH \longrightarrow C\text{—}O^\bullet + H\text{—}OH.$$

On the other hand, the action of H_2O_2—Fe^{++} mixture on 2 : 3-butylene glycol, HO—CHMe—OH, yields much more diacetyl than acetaldehyde; C—H bonds are attacked and Hg^{++} is reduced.

I would suggest that whilst the reaction,

$$R''CH\begin{matrix}\diagup H\\ \diagdown O\text{—}H\end{matrix} + {}^\bullet OH \longrightarrow R''\dot{C}\diagdown O\text{—}H + H\text{—}OH,$$

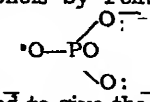
is rapid, exothermic and irreversible, the alternative process,

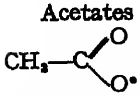
$$R''CH\text{—}O\text{—}H + {}^\bullet OH \rightleftharpoons R''CH\text{—}O^\bullet + H\text{—}OH,$$

which we had to invoke to explain our "dilution effect" (p. 184) can also occur as a reversible chain-transfer process. The oxidation of pinacol then shows that the radical HO—$\dot{C}Me_2$—CMe_2—$O^\bullet$ can undergo disproportionation, giving a diradical which effects glycol-splitting. It is premature to say whether all other cases of glycol-splitting occur similarly, or whether the diradical is formed by a single-stage breakdown of a cyclic compound as suggested by Criegee.

We have preliminary evidence to indicate that changes of pH, and

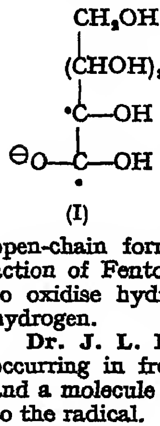
[3] *Trans. Faraday Soc.*, 1941, 37, 779; 1946, 42, 185.

the additions of other anions can, by altering the equilibria concerned in chain transfer, greatly alter the relative ease of the C—H and the O—H attacks in aqueous solutions. For instance, an increase of pH seems to favour glycol-splitting, possibly by weakening —OH links, or by facilitating electron release from C—$\bar{O}$:. Again the addition of phosphates decreases the efficacy of oxidation of alcohols by Fenton's reagent, probably by replacing •OH by the less active  radical-ion.

Acetates too would be expected to give the resonance-stabilised radical  and therefore might be much less active than hydroxyl towards C—H links, but still might be capable of chain transfer with R—O—H.

All these questions of relative reactivity and chain transfer need to be examined on a quantitative basis before we can be sure of the exact mechanisms of all our oxidations. *It is well to remember too that even* in cold solutions both the Criegee and the Malaprade reagents can be used to oxidise organic compounds of other types than glycols.

Dr. T. P. Nevell (*Manchester*) said: Some work about to be submitted for publication suggests that Dr. Dewar's objections to a free-radical mechanism for the oxidation of α-glycols by periodate are not justified. In the oxidation of glucose by periodate, the final products of which are formaldehyde and formic acid, relatively stable intermediate products which are themselves oxidising agents have been detected. It is postulated that these substances are resonance-stabilised ionic free radicals of the type (I) which can be obtained by the abstraction of two atoms of hydrogen from the hydrated open-chain form of glucose. Another point of similarity between the action of Fenton's reagent and periodate is the ability of both reagents to oxidise hydroquinone to quinone by the removal of two atoms of hydrogen.



(I)

Dr. J. L. Bolland (*Welwyn*) said: A type of reaction commonly occurring in free-radical chemistry is the interaction between a radical and a molecule in which a hydrogen atom is transferred from the molecule to the radical. The detailed chemical structure of the molecule concerned will obviously influence the ease with which a hydrogen atom may be abstracted from it, and in several contributions to the discussion effects of the kind are traced (e.g. [4-7]). A further experimental method of measuring the rate of such hydrogen-transfer reactions emerges from a study of the kinetics of oxidation of a series of non-conjugated olefins, in presence of a radical-producing chain initiator like benzoyl peroxide: without introducing any unjustified assumption it is possible to determine for each olefin the relative rate of the oxidation chain-propagation step:

$$RO_2^- + RH \rightarrow RO_2H + R^- \quad k_3$$

(where RH and RO_2H represent an olefin and the corresponding α-methylenic hydroperoxide respectively, R^- the radical resulting from abstraction of one α-methylenic hydrogen atom and RO_2^- the corresponding peroxide radical). Differences in the rate of this reaction for different olefins may be attributed almost entirely to variations in the R—H bond strength, since the influence of the structure of the hydrocarbon portion on the reactivity of the RO_2^- radical is likely to be of only secondary importance.

[4] Merz and Waters, this Discussion, p. 179.
[5] Bolland and ten Have, *ibid.*, p. 252.
[6] Gregg and Mayo, *ibid.*, p. 328.
[7] Steiner, *ibid.*, p. 87.

As an example of the results obtained by the method we may quote relative figures for the reaction velocity coefficient k_3 for six hydrocarbons, which illustrate the influence of methyl substitution at a double bond on the ease of α-methylenic hydrogen removal. The first three hydrocarbons are aliphatic, the remainder allyl benzene derivatives.

The increase in k_3 with increasing degree of substitution observed in both series of hydrocarbons is paralleled by a decrease in activation energy (ΔE_3), the most probable values of which are included in the table. There is a definite increase in frequency factor as the energy of activation increases, in conformity with the observations of Gregg and Mayo [6] on the very similar transfer reaction in polymerisation.

Qualitatively these results can easily be accounted for by consideration of the resonance energy of the different R^- radicals involved, or by the application of molecular-orbital concepts; [8] quantitative consideration of these and other similar simple substitutive factors represents an interesting and important problem.

Olefin.	k_3 (relative).	ΔE_3 (kcal./mole.).
$R.CH_2.CH{=}CH_2$	(1)	(0)
$R'.CH_2.CH{=}CH.CH_3$	3·6	1·7
$R''.CH_2.CH{=}C.(CH_3)_2$	18	3·9
$\phi.CH_2.CH{=}CH_2$	6·0	2·4
$\phi.CH_2.CH{=}CH.CH_3$	29	4·5
$\phi.CH_2.CH{=}C.(CH_3)_2$	98	6·0

Dr. J. Weiss (*Newcastle*) said: The paper presented by myself should be regarded as a first attempt to describe the mechanism of the reaction with a minimum number of elementary processes sufficient to bring out all the essential features. Thus, at this stage, the influence of pH and of other factors has not been discussed in detail. In the case of *quantitative* measurements as carried out by Haber and Weiss (loc. cit.) in the system H_2O_2—Fe^{II}, it is most essential to ensure—by special devices—that the mixing velocity is greater than the (chemical) reaction velocity. It is clear that if this condition is not fulfilled the initial concentrations are not properly defined.

Dr. J. Y. Macdonald (*St. Andrews*) said: There is reason to believe that some of the complexities of the decomposition of silver oxalate [9] may be explained by assuming that a semi-oxidised oxalate ion of the type postulated by Weiss is formed, the reaction being

$$C_2O_4^{=} \rightleftharpoons C_2O_4^{-} \rightarrow 2CO_2.$$

The fact that this ion is part of a solid structure while that of Weiss is in solution, however, may make a fundamental difference. The oxalate ion is unstable in the vapour phase, but becomes stable when it is in the strong positive electric field which is provided by the neighbouring cations in the crystal lattice, and by the water dipoles in aqueous solution. The same thing is to be expected in the case of the semi-oxidised ion, whose stability (i.e. life period) will probably vary with the strength of the surrounding field, i.e. with the dipole moment of the solvent. This is a matter of practical importance when studying, say, alcohol-water mixtures whose composition is varying. The above considerations apply to other unstable ions such as SO_4^-.

Dr. N. Uri (*Leeds*) (*communicated*): The Haber-Weiss [10] chain mechan-

[8] Walsh, *ibid.*, this Discussion, p. 18.

[9] Macdonald and Sandison, *Trans. Faraday Soc.*, 1938, 34, 589, etc.; Tompkins, *ibid.* (in press).

[10] *Proc. Roy. Soc. A*, 1934, 147, 332.

ism has no doubt brought much light upon a great number of confusing experimental phenomena, for which only very unsatisfactory theories, as the formation of higher iron peroxides, could be put forward. Confirmatory evidence (though likewise indirect) for the formation of OH radicals in the $Fe^{++}—H_2O_2$ system has also recently been presented by Baxendale, Evans and Park.[11] There are, however, many points yet to be clarified, especially with regard to the kinetics of the chain reaction. These apply also to the present paper. With the assumption of the stationary state one should expect that the *rate* of CO_2 evolution or calomel formation is entirely independent of the ferrous ion concentration. This conclusion has not been experimentally verified. The following question arises: why is oxalic acid not activated (assuming the Haber and Weiss mechanism) in the system $Fe^{+++}—H_2O_2$, even in the dark, according to the following equations:

$$Fe^{+++} + HO_2^- = Fe^{++} + HO_2 \qquad (1)$$
$$HO_2 + H_2O_2 = O_2 + H_2O + OH \qquad (2)^*$$
$$OH + C_2O_4^{--} = OH^- + C_2O_4^- \qquad (3)$$

Should one expect that O_2 evolved in (2) inhibits the chain reaction with $C_2O_4^-$ by $C_2O_4^- + O_2 = 2CO_2 + O_2^-$ (eqn. (17) in the paper presented)? This inhibitory mechanism is, however, hardly adequate, when a system containing H_2O_2 is considered, since O_2^- (or HO_2) may then react with H_2O_2 to give again OH and O_2, producing CO_2 according to (3) and (17); in other words the inhibitory reaction would be part of another chain mechanism for the oxidation of oxalic acid.

Moreover, when the crystallised $K_3[Co(C_2O_4)_3]$ is dissolved in water, it is a very active catalyst for the decomposition of hydrogen peroxide, without the oxalate, however, being oxidised during the O_2 evolution. The cobaltic oxalate complex decomposes only very slowly at room temperature. This phenomenon is difficult to explain with the theories put forward in the present paper for OH radicals as probable chain carriers of the H_2O_2 decomposition as well as cobaltic ions should initiate a rather quick oxalate destruction.

Finally, it would be interesting to learn whether the chain length of the reactions leading to CO_2 evolution or to calomel formation can be considerably increased by adopting different mixing conditions (compare the "centrifugal" and the "pouring" experiments reported by Haber and Weiss [10]). This point has not as yet been mentioned in any of the numerous papers dealing with the structure of "active" oxalic acid.

Dr. J. Weiss (*Newcastle*) (*partly communicated*): In the reaction between $H_2O_2—Fe^{II}$ and different substrates one encounters two essentially different types of reactions.[12]

CASE (*a*). The acceptor is oxidised *only* by the system $(H_2O_2 + Fe^{II})$ and the oxidation of the acceptor comes to a stop when all the Fe^{II} has been transformed into Fe^{III}. This is the case with most of the acceptors (e.g. formic acid, alcohols, H_3AsO_3).

Case (*b*). The acceptor is readily oxidised by ferric salts alone (but not by H_2O_2 alone). In this case one finds—superimposed on the action of the OH radicals as in (*a*)—that the action of the hydrogen peroxide consists chiefly in the repeated re-oxidation of Fe^{II} to Fe^{III}. This is the case with acceptors such as hydroquinone, catechol, etc.

The answer to Uri's question is contained in my paper. For the formation of calomel, a suitable oxidising agent is required to start the

[11] *Trans. Faraday Soc.*, 1946, 42, 155.

* HO_2 in eqn. (2) has been later replaced by O_2^-. It is, however, well established that the rate of H_2O_2 decomposition catalysed by Fe^{+++} ions is inversely proportional to $[H^+]$ and not to its square as it might be derived from the latter assumption.

[12] Cf. Weiss, *J. Physic. Chem.*, 1937, 41, 1107.

process and the same oxidising agent generally acts as inhibitor of the chain reaction. Only if a certain balance is struck between these two processes can the formation of calomel take place. The inhibition by oxygen (or other oxidising agents) is due not only to a reaction with $C_2O_4^-$, as Uri suggests, but the reaction with Hg^+ is of equal importance. Ferric ions themselves are known to be strong inhibitors for the calomel formation (cp. Rosevaere, J. *Amer. Chem. Soc.*, 1930, **52**, 2612) while it is not certain whether they initiate the reaction, even in the presence of hydrogen peroxide. I am not aware, however, of any experiments which show that calomel is definitely not formed under these conditions.

In the presence of potassium cobalti-oxalate, it is quite possible that at low concentrations of oxalate the decomposition of hydrogen peroxide predominates: it follows clearly from the theory that there is always a competition for the oxidising radicals between the oxalate and the hydrogen peroxide.

Dr. W. A. Waters (*Oxford*) said: In connection with Dr. Weiss's study of the active radical derived from oxalic acid, I wish to report that in the Dyson Perrins Laboratory Mr. Merz has recently found that a similar reduction of mercuric chloride is exhibited in our alcohol—H_2O_2 systems. This is evidently due to the reaction

$$CH_3—\dot{C}H—OH + Hg^{++} \longrightarrow Hg^+ + CH_3—\overset{+}{C}H—H \longrightarrow CH_3—CH{=}O + H^+$$

and affords excellent substantiation for the view that the oxidation of alcohols normally involves attack on the C—H bond, since a reaction such as

$$CH_3—CH_2—O^\bullet + Hg^{++} \longrightarrow CH_3—CH_2—\overset{+}{O} + Hg^+$$

is quite out of the question.

The radicals derived from primary and secondary alcohols, including ethylene glycol and 2 : 3-butylene glycol, and also the radical derived from acetaldehyde, all have this power of reducing mercuric chloride, but significantly enough the radicals involved in the oxidation of pinacol, HO—CMe_2—CMe_2—OH, do not affect mercuric chloride. Thus the reduction of a mercuric salt seems to be a good test for the presence of a trivalent carbon radical in aqueous solution. The reaction is a chain-breaking process which may help us to determine the absolute rates of our free radical-oxidation processes.

With respect to permanganate oxidation it is worth recalling that oxidation curves very similar to those of page 194 were reported by Doroshevskii and Bardt [13] in 1914 for the permanganate oxidation of alcohols in the presence of ferrous salts.

In the past year Mr. R. D. Brearley, of Oriel College, and I have been carrying out exploratory studies of permanganate oxidations of organic compounds which show that "reduction-activation" is quite common in this complex system. For instance, though $KMnO_4$ gives a stable solution in acetone, when such solutions are used for oxidising other organic compounds then some concurrent oxidation of the acetone frequently occurs. Thus some intermediate oxidation product, derived from $KMnO_4$, or from organic substances such as cyclohexanol, must be capable of attacking the C—H bonds of acetone. This is *not* the •OH radical since the H_2O_2—Fe^{++} system has scarcely any action on acetone. We may therefore have to take into consideration other transient intermediates than Mn^{3+}.

Dr. J. Weiss (*Newcastle-on-Tyne*) (*communicated*): With regard to the paper of Haber and Weiss [14] published in 1934, it has been found now that certain simplifications can be introduced so that all the reactions between

[13] *J. Russ. Physic. Chem.*, 1914, 46, 754.

[14] Haber and Weiss, *Proc. Roy. Soc. A.*, 1934, 147, 332; also *Naturwiss.*, 1932, 20, 948.

iron salts and hydrogen peroxide can be described to a good approximation by the following five equations :

$$
\begin{array}{lll}
(1) & Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH & (k_1) \\
(2) & H_2O_2 + OH \rightarrow H_2O + HO_2 & (k_2) \\
(3) & H_2O_2 + HO_2 \rightarrow H_2O + O_2 + OH & (k_3) \\
(4) & Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- & (k_4) \\
(5) & Fe^{3+} + HO_2^- \rightarrow Fe_2^+ + HO_2 & (k_5) \\
(5') & Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^- & (k'_5)
\end{array}
$$

It is known that hydrogen peroxide reacts with ferrous salts in a rapid reaction which practically comes to a stop when all the ferrous salt has been transformed into ferric salt. A definite amount of H_2O_2 has then disappeared per one mole of ferrous salt used up corresponding to the (relatively short) time-interval in which the practically complete oxidation of ferrous to ferric salt has taken place. As shown previously, reactions (1), (2), (3) and (4) are adequate to describe the course of the reaction. Starting with a "neutral" solution, H^+ ions are used up in the reaction and the ferric ions are hydrolysed or precipitated as basic salts and are thus eliminated from the reaction. It should be pointed out, however, that eqn. (4) can be replaced formally by eqn. (5') although the fact that one can have the simple stoichiometry comprising reactions (1) and (4) would seem to favour (4).

From the eqn. (1), (2), (3) and (4), it is possible to derive an expression for the mean consumption ratio ($\bar{n}$), i.e. moles of H_2O_2 decomposed by one mole of Fe^{II} salt which is given by : *

$$\bar{n} = \frac{-\Delta(H_2O_2)}{-\Delta(Fe^{II})} = \frac{\int_0^t -\frac{d(H_2O_2)}{dt}dt}{\int_0^t -\frac{d(Fe^{2+})}{dt}dt} = 0{\cdot}5 + \frac{k_2}{k_4}\frac{\int_0^t [H_2O_2]^2 dt}{\int_0^t [H_2O_2][Fe^{2+}]dt}.$$

If the time-dependent concentrations of the reactants are replaced by suitable mean concentrations $(H_2O_2)_m$ and $(Fe^{2+})_m$ one obtains :

$$\bar{n} = 0{\cdot}5 + \frac{k_2}{k_4}\frac{(H_2O_2)_m}{(Fe_2^{2+})_m}$$

However, the above scheme of reactions cannot be quite complete as it is known that the chain length decreases with increasing H^+ concentration. This means that the chain propagation is to some extent inhibited by H^+ ions. This could point to participation of HO_2^- or O_2^- in some of the chain reactions. It is also possible that some of the chain-breaking processes are accelerated by H^+ which could be due to the participation of $H_2O_2^+$ instead of HO_2, or H_2O^+ instead of OH, in certain chain-breaking processes. The interactions of two radicals have been excluded from the above scheme mainly for reasons of simplicity but there can be no doubt that they are of some importance, e.g. at sufficiently low Fe^{2+} concentrations and also, for instance, in the photochemical decomposition of hydrogen peroxide.

In acid solutions when the ferric salt remains in solution, the rapid reaction between ferrous salt and H_2O_2 is followed by the very much slower (catalytic) decomposition of hydrogen peroxide. As was shown previously,[1] in this reaction the ferric salt is periodically reduced (and reoxidised) in the course of the reaction and a stationary state is established, which normally is situated almost completely on the ferric side.

Recent investigations have shown that the course of this catalysis can be described by the above equations *without* the inclusion of eqn. (14)

* This expression should replace the one given previously. (cf. also Weiss, *Trans. Faraday Soc.*, this Discussion p. 188).

of the previous paper.[11] It has also been confirmed that Fe^{3+} ions enter into the mechanism and not any of their hydrolysis products (e.g. $Fe(OH)^{2+}$). However, as pointed out above, the stationary Fe^{2+} concentration is very low in this case and in a region where—according to the previous discussion[14]—the interaction of two radicals can already assume importance in the chain-breaking processes (e.g. the reaction, $HO_2 + OH \rightarrow H_2O + O_2$).

In an endeavour to find again the *minimum* number of equations which are adequate to describe the course of the reaction one observes that eqn. (3), (4), (5) and (5′) are sufficient to deal with the ferric ion catalysis in acid solution. This then corresponds to the following stoichiometry:

$$\begin{aligned} H_2O_2 &= H^+ + HO_2^- \\ Fe^{3+} + HO_2^- &= Fe^{2+} + HO_2 \\ H_2O_2 + HO_2 &= O_2 + H_2O + OH \\ Fe^{2+} + OH &= Fe^{3+} + OH^- \\ OH^- + H^+ &= H_2O \\ \hline 2H_2O_2 &= 2H_2O_2 + O_2 \end{aligned}$$

For the stationary state of the radicals one obtains in the usual way:

$$+\frac{d(O_2)}{dt} = -\frac{1}{2}\frac{d(H_2O_2)}{dt} = k_3[H_2O_2]\frac{k_5[Fe^{3+}][HO_2^-]}{k_3[H_2O_2] + k'_5[Fe^{2+}]},$$

which for the low $[Fe^{2+}]$ present in the solution may reduce, for $k'_5[Fe^{2+}] \ll k_3[H_2O_2]$ to:

$$\frac{d(O_2)}{dt} \simeq k_5[Fe^{3+}][HO_2^-] = k_5K_{H_2O_2}\frac{[Fe^{3+}][H_2O_2]}{[H^+]},$$

($K_{H_2O_2}$ = diss. constant of hydrogen peroxide) which is in agreement with the experimental facts.

Dr. N. Uri (*Leeds*) (*communicated*): In connection with Dr. Weiss's proposal (p. 211) to divide the systems Fe^{II}—H_2O_2-acceptor into two groups, it would appear that a division into three different types is preferable.

CASE (*a*). The acceptor is oxidised by both the Fe^{II}—H_2O_2 and the Fe^{III}—H_2O_2 system but neither by ferric ions nor by hydrogen peroxide alone. This is the case with most of the acceptors, such as alcohols, organic hydroxy-acids, etc. When all the Fe^{II} has been transformed into Fe^{III}, the oxidation comes to a stop *only* when the solution is either strongly acid or the ferric ions are withdrawn by precipitation or complex formation. It should be added that the *rate* of oxidation is in all cases higher with the Fe^{II}—H_2O_2 system than with Fe^{III}—H_2O_2.

CASE (*b*), as proposed by Weiss (p. 211).

CASE (*c*). The acceptor is oxidised by H_2O_2 + Fe^{II} but is not affected by H_2O_2 + Fe^{III}. An example for this case is oxalic acid which is dealt with in a paper presented by Weiss in this discussion. Case (*c*) applies to those systems, in which O_2 acts as an inhibitor of the acceptor-oxidation.

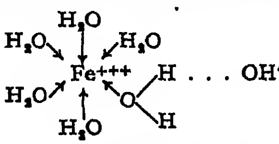
As a general rule, it would appear that in cases where O_2 acts as an inhibitor, the acceptor reaction does not occur when HO_2 and not OH is the radical *primarily* formed in the system. This has been shown for polymerisation systems as well as for Fe^{III}—H_2O_2-oxalate and Co^{III}—H_2O_2-oxalate.

It might be added that with regard to the decomposition of H_2O_2, the catalytic activity of ferric ions or cupric ions can be considerably increased by their transformation into certain labile co-ordination compounds such as chloro-complexes, but even under these conditions and with a continuous stream of nitrogen passing through the system, no polymerisation has occurred, when acrylonitrile had been previously added to the reaction mixture (unpublished experiments by N. Uri). The more difficult aspect of the problem is the mechanism of the inhibition reaction.

Prof. A. R. Ubbelohde (*Belfast*) said: With regard to the reactions involving electron transfer, it is important to remember that in the aqueous solution we do not normally deal with "naked" positive ions such as Fe^{+++}, Mn^{+++}, etc., but with co-ordination complexes. This has a bearing on the argument about the ease with which an electron can be transferred from the *d* quantum groups of the transitional ion. For example, in investigations on the rate of oxidation [15] it was anticipated that electron-transfer reactions should be much more rapid than those involving co-valent linkages, and, for example, that reduction of the manganic ion Mn^{+++} would be much more rapid than the reduction of the permanganate MnO_4'. Experiments showed that this reduction was, in fact, much more rapid, but it also showed that the "manganic ion" was present as a *complex ion* with negative charge. In fact, we must normally expect the electron to be transferred through a co-ordinated sheath of molecules around the atom under consideration. It is interesting to consider under what circumstances this transfer can take place very quickly. Two illustrations may be given.

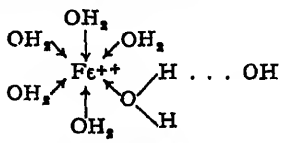
(1) When the co-ordinated molecules are H_2O molecules, it may be that certain radicals such as OH are *especially* favoured for the transfer of electrons in a series of bond switches [16] facilitated by the specific formation of hydrogen bonds.

An "oxidation transfer" of electrons may be symbolised in terms of an electron switch across co-ordinated H_2O, to an OH ion:



Stage I.

OH′ ion approaches the complex ferric ion and forms a hydrogen bond.



Stage II.

OH radical leaves the complex ferrous ion.

Reduction transfer is the reverse of the above.

(2) Alternatively, sheaths of co-ordinated molecules in complex ions may act quite generally as conductors of electricity, or as insulators, depending on their electronic structure. For example, H_2O molecules apparently act as conductors. But other more stable complexes such as $\left[Fe(CN)_6\right]^{++++} \rightarrow \left[Fe(CN)_6\right]^{+++}$ may perhaps involve a "slow" electron switch. It would be interesting to search for co-ordination complexes in which the electron switches are "insulated" from the surroundings.

Mr. J. E. B. Randles (*Birmingham*) said: With reference to the remarks of Prof. Ubbelohde concerning the facility of electron transfer to, or from, a "complex" or solvated ion, I can give some information about this process when it occurs at the surface of an electrode in a solution. Measurements made by an oscillographic method [17] indicate that reactions such as $Fe(C_2O_4)_3^{--} \rightleftharpoons Fe(C_2O_4)_3^{---} +$ and $e\ Fe(CN)_6^{--} \rightleftharpoons Fe(CN)_6^{---} + e$ are extremely rapid and must have almost zero activation energy whereas electron transfers to, or from, hydrated ions are often comparatively slow,

$$\text{e.g.} \qquad Fe_{aq}^{++} - Fe_{aq}^{+++},\ V_{aq}^{++} - V_{aq}^{+++},\ Cr_{aq}^{++} - Cr_{aq}^{+++},$$

(the last being extremely slow). Although the experimental data are as yet insufficient for a definite statement I think that it is probably the case that electron transfer to, or from, an ion occurs without appreciable activation

[15] Ubbelohde, *J. Chem. Soc.*, 1935, 1605.

[16] Cf. Ubbelohde, *loc. cit.*, 1607.

[17] Randles, *Trans. Faraday Soc.*, 1947, 44A (in press).

energy unless some re-arrangement in the immediate sheath of co-ordinated ions or molecules accompanies the change of charge.

Dr. R. A. Robinson (*Auckland*) (*communicated*): Dr. Ubbelohde's suggestion that the effect of the water molecules around the ions in the Fe^{++}—Fe^{+++} system might be obviated by working with the $Fe(CN)_6^{---}$ — $Fe(CN)_6^{----}$ system, prompts the further suggestion that this object could also be achieved by surrounding the cations with ethylenediamine molecules. Some experimental evidence has been obtained recently that the " solvation " effect between zinc ions and water molecules can be destroyed if the cation is present as $[Zn\ 3en]^{++}$. Mr. E. O. Farrelly[18] has measured the isopiestic ratio between NaCl and $[Zn\ 3en](NO_3)_2$ from which the following osmotic coefficients can be calculated and compared with those of zinc nitrate.[19]

m	0·1	0·2	0·3	0·5	0·7	1·0	1·5	2·0	2·5	3·0	3·5	4·0
$\phi[Zn\ 3en](NO_3)_2$	0·972	0·888	0·831	0·755	0·705	0·653	0·608	0·594	0·591	0·595	0·600	0·688
$\phi[Zn(NO_3)_2]$	0·862	0·873	0·890	0·934	0·982	1·064	1·209	1·355	1·506	1·664	1·817	1·960
$\phi[Zn\ 12\ H_2O](NO_3)_2$	0·843	0·835	0·833	0·833	0·833	0·834	—	—	—	—	—	—

In the most dilute solutions the osmotic coefficients are higher than would be expected ; this is probably due to some dissociation of the complex ion. In the more concentrated solutions, however, the coefficients are very low, comparable with those of sodium sulphate and in marked contrast to those of $Zn(NO_3)_2$. Mr. R. H. Stokes and I have advanced a " hydration " hypothesis leading to the equation :

$$-\log \gamma = 0{\cdot}5092\, z_1 z_2 \sqrt{\mu}/(1 + 0{\cdot}3286\, a \sqrt{\mu}) + n/\nu \log a_w + \log [1 - 0{\cdot}018\,(n - \nu)m]$$

for the activity coefficient in water at 25° of a salt dissociating into ν ions with an effective hydration number of n. The experimental data for $Zn(NO_3)_2$ are satisfied by $a = 5{\cdot}13$, $n = 12{\cdot}0$. It is therefore better to compare the osmotic coefficient of $[Zn\ 3en](NO_3)_2$ with that of $[Zn\ 12\ H_2O](NO_3)_2$, the latter being calculated from :

$$\phi[Zn\ 12\ H_2O](NO_3)_2 = (55{\cdot}51 - 12m)/55{\cdot}51\ \ \phi[Zn(NO_3)_2]$$

and given in the last line of the above table. It is evident that a considerable proportion of the difference between the " aquo " and the ethylenediamine salt is explained by the fact that no account is taken of the hydration effect in calculating the usual stoichiometric osmotic coefficient of the former. That the values for the ethylenediamine salt are lower, even after allowance is made for the hydration effect in the " aquo " salt indicates that it has a smaller mean ionic diameter, of the order of 3·5 A. ; the ethylenediamine molecules are more tightly packed than the water molecules. The important fact is that ϕ for $[Zn\ 3en](NO_3)_2$ is not greater than that for the aquo salt ; it follows that in the former interaction between the complex cation and solvent molecules is small in extent if not entirely negligible. If the same is true for the Fe^{++}—Fe^{+++} system, then ethylenediamine or one of its homologues should be of use in screening the ions from solvent molecules.

[18] *Thesis* (University of N.Z. 1945). Solutions of the following molalities of $[Zn\ 3en]\ (NO_3)_2$: and NaCl respectively, were isopiestic : 0·1403, 0·2127 ; 0·3077, 0·4180 ; 0·3238, 0·4362 ; 0·3915, 0·5002 ; 0·5580, 0·6667 ; 0·9283, 0·9828 ; 1·074, 1·099 ; 1·736, 1·611 ; 1·758, 1·632 ; 2·427, 2·181 ; 2·897, 2·527 ; 3·467, 3·026 ; 4·196, 3·526 ; 4·481, 3·762.

[19] Stokes and Levien, *J. Amer. Chem. Soc.*, 1946, 68, 333.

Prof. M. G. Evans (*Leeds*) said: We naturally realise, as Prof. Ubbelohde has pointed out, that in these ionic reactions the ferrous and ferric ions are solvated. In picturing the detailed mechanism of such reactions one must consider the role played by the water molecules in the solvation shell of the ions. The energy of replacement of the molecules of the solvation shell by the reacting partner is an important factor in determining the activation energy of reaction, and moreover, changes in the entropy of solvation are reflected in the entropy changes of the reaction. As an example of this we can cite the large entropy change accompanying the reaction [20]

$$Cl^- + Cl{-}OH \rightarrow Cl{-}Cl + OH^- \qquad \Delta S = -23 \text{ cal./}^\circ.$$

This large entropy change arises practically entirely from the stronger solvation of the OH ion as compared with that of the chlorine ion. This type of entropy change reveals itself not only in the equilibrium constant but also in the velocity constant of the reaction. Thus in the reaction between ferrous ions and hydrogen peroxide, we attribute the low temperature-independent factor: $k = 1{\cdot}78 \times 10^9 . e^{-10{,}100/RT}$ to the formation of the heavily solvated hydroxyl ion.[21]

The energy of co-ordination of water molecules around ferrous and ferric ions is included in the oxidation-reduction potential of that system. Changes in the nature of the complexes, for example, by changing to ferrous $\alpha\alpha'$ di-pyridyl and phenanthroline complexes or to ferrocyanide, bring about changes in the oxidation-reduction potential of the system and Mr. Cowling has shown that such changes very markedly affect the rate of the primary electron-transfer reaction, and in fact these two effects, namely, the oxidation-reduction potential and the velocity constant can be directly related.

Dr. N. Uri (*Leeds*) (*communicated*): The interpretation given by Prof. Ubbelohde (p. 215) to the electron-transfer reaction involving solvated ferric ions and hydroxyl ions apparently does not take into account the formation of $[Fe(H_2O)_5 . (OH)]^{++}$ in aqueous solution.[22] This latter ion has, according to Rabinowitch,[23] a characteristic electron-transfer spectrum and can hardly be disregarded. The rate of electron transfer is certainly dependent on the concentration of this complex ion which varies with the hydrogen ion activity of the solution. It would not seem improbable that with Mn^{+++} also, the first step is the formation of $[Mn(H_2O)_5(OH)]^{++}$.

Dr. J. Weiss (*Newcastle*) said: I do not think that the experiments of Dr. George have any bearing on the mechanism of the hydrogen peroxide reaction. It is quite clear from his paper that the experiments were carried out in a *heterogenous* system—*solid* KO_2 *in* H_2O_2 *solutions*. In some cases the conditions were quite complex when iron salts were added which were partly precipitated in the alkaline environment of the KO_2 particles. It is known from the classical work of Noyes and Whitney and of Nernst and his school that in a heterogenous system of this type, when the (true) chemical reaction at the interface is a fast process, that diffusion processes are the time-determining factors. Therefore, the experiments of George do not allow any conclusions to be drawn with regard to the specific rate of the interaction between H_2O_2 and HO_2 or O_2^-, just as no one could claim to measure the true velocity of neutralisation by determining the rate of reaction between e.g. solid MgO and HCl: in both cases one measures only some rates of diffusion.

I should like to add that the scheme of reactions which I put forward

[20] Morris, *J. Amer. Chem. Soc.*, 1946, 68, 1692.
[21] Baxendale, Evans and Park, *Trans. Faraday Soc.*, 1946, 42, 155.
[22] Rabinowitch and Stockmayer, *J. Amer. Chem. Soc.*, 1942, 64, 335.
[23] *Rev. Mod. Physics*, 1942, 14, 112.

in 1935 [24] which, in addition to the hydrogen peroxide reactions, consists of the following processes:

$$\begin{aligned} O_3 + OH^- &= O_2^- + HO_2 \\ O_3 + HO_2 &= 2O_2 + OH + 33 \text{ kcal.} \\ O_3 + OH &= O_2 + HO_2 + 34 \text{ kcal.} \\ HO_2 + OH &= O_2 + H_2O + 70 \text{ kcal.} \end{aligned}$$

was taken over fully by Taube and Bray (loc. cit.) into their paper published in 1940, so that Bray had in fact withdrawn the objections which he had raised in his earlier paper in 1938.

I also had shown previously that the interaction between ozone and hydrogen peroxide leads to a consumption ratio $\frac{\Delta(O_3)}{\Delta(H_2O_2)} \sim 1$, only for low ratios of the concentrations $\frac{(O_3)}{(H_2O_2)}$, while for higher values of this ratio one finds $\frac{\Delta(O_3)}{\Delta(H_2O_2)} > 1$, values up to ~ 20 having been observed.

Dr. Philip George (*Leeds*) (*communicated*): At the Sept. meeting of the American Chemical Society, Dr. J. Kleinberg reported experiments on the oxidation of sodium in liquid ammonia at $-77°$ C. in which he showed by gasometric methods that sodium superoxide is the first oxidation product This explains the early observation of Joannis [25] who obtained a product corresponding to Na_2O_3 by oxidation of sodium in liquid ammonia at $-50°$ C The solid oxide obtained by Kleinberg after evaporation of the ammonia contained roughly 50 % of NaO_2. This may be compared with the 10 % which I have found in commercial samples of " sodium peroxide " prepared by burning sodium in oxygen.

Dr. J. N. Agar and Dr. F. S. Dainton (*Cambridge*) (*communicated*): In the photochemical decomposition of aqueous solutions of hydrogen peroxide, there can be little doubt that the hydroxyl radicals produced in the primary act react according to $OH + H_2O_2 \rightarrow HO_2 + H_2O$, thus fulfilling their usual function of H-atom abstraction. There are good reasons [26] for regarding this reaction as very efficient, taking place at almost every collision. The second step in the propagation of the reaction chain can only be

$$HO_2 \text{ (or } O_2^-) + H_2O_2 \rightarrow H_2O \text{ (or } OH^-) + O_2 + OH.$$

Sector experiments [27] and quantum-yield measurements indicate that the collision yield for this reaction is very low, and we may tentatively assign an energy of activation $\nless$ 10 kcal. In this connection, it is worth noting that Lewis and von Elbe [28] consider that the energy of activation is 14 kcal. for the reaction

$$HO_2 + H_2O_2 \rightarrow H_2O + O_2 + OH$$

in the gas phase.

Taylor and Anderson [29] have found that alkali inhibits the photolysis of aqueous H_2O_2, and we are led to conclude that this reaction becomes less probable in alkaline media, i.e. with increasing dissociation of $HO_2 \rightarrow H^+ + O_2^-$ and $H_2O_2 \rightarrow H^+ + HO_2^-$. Indeed, in *strongly* alkaline solutions of HO_2 and H_2O_2, the concentration of undissociated molecules must be negligibly small compared with O_2^- and HO_2^- (taking $K_{HO_2} = 10^{-7}$ and $K_{H_2O_2} = 10^{-12}$), and, since no feasible oxygen-producing reaction

[24] Weiss, *Trans. Faraday Soc.*, 1935, 31, 668.
[25] Joannis, *Compt. rend.*, 1893, 116, 1370.
[26] Oldenberg, *J. Chem. Physics*, 1936, 4, 642, 741.
[27] Allmand and Style, *J. Chem. Soc.* 1930, 596, 606.
[28] Lewis and v. Elbe, *J. Chem. Physics*, 1942, 10, 366.
[29] Taylor and Anderson, *J. Amer. Chem. Soc.*, 1923, 45, 1210.

can be formulated between O_2^- and HO_2^-, it appears that under such conditions the O_2^- radicals are destroyed by other means, e.g.,

$$2O_2^- + H_2O \rightarrow O_2 + HO_2^- + OH^-,$$

possibly according to equations (1*d*-*f*) given by George.

Owing to the rapidity with which the reaction between KO_2 and aqueous solutions takes place, the concentrations of OH^- and HO_2^- in the immediate vicinity of the solid particles of KO_2 must reach very high values; OH^- and HO_2^- originate, of course, from the K_2O and K_2O_2 content of the solid, as well as from the decomposition of KO_2 by water. It is very probable that these concentrations are so high that the addition of acid, alkali or hydrogen peroxide to the bulk of the solution, in amounts such as those shown in Table II, has little effect on the conditions close to the solid surface.

The high alkalinity at the interface will tend to inhibit the reaction between peroxide and O_2^-, and it is therefore reasonable to expect that the majority of the HO_2^- ions will escape by diffusion into the bulk of the solution. On the other hand, it is unlikely that the O_2^- ions will succeed in so doing, as the conditions are favourable for them mutually to destroy one another in, or near, the interface. It is thus improbable that the chain decomposition of H_2O_2 will be initiated to any appreciable extent in the less alkaline parts of the solution distant from the KO_2 particle.

It seems to us, therefore, that the conclusion from Dr. George's experiments is not that " under these experimental conditions the chain-propagation reaction proposed by Haber and Weiss . . . does not occur", but that under the experimental conditions the number of $O_2^- : H_2O_2$ encounters is negligibly small and the HO_2 or O_2^- radicals are otherwise destroyed. We see no valid reason in these experiments for abandoning the Haber-Weiss reaction

$$O_2^- + H_2O_2 \rightarrow OH^- + O_2 + OH$$

as the oxygen-producing process in the decomposition catalysed by Fe^{++}, Fe^{+++} or catalase, or photochemically.

Dr. Philip George (*Leeds*) (*communicated*): As Dainton and Agar point out, there is little doubt that reaction (1)

$$HO + H_2O_2 \rightarrow H_2O + HO_2 \quad . \quad . \quad . \quad (1)$$

is very efficient, and so in those reactions of hydrogen peroxide in which oxygen is evolved, it is important to know whether reaction (2)

$$O_2^-(HO_2) + H_2O_2 \rightarrow O_2 + OH^-(H_2O) + HO \quad . \quad . \quad (2)$$

is comparably efficient and can only be held in check by powerful chain-breaking reactions, or whether it occurs relatively inefficiently so that, with other appropriate reactants present (ozone, metal ions, etc.), the oxygen is evolved by alternative reaction paths. If the H_2O_2 formed *in situ* from the KO_2 and K_2O_2 had been rapidly decomposed by the remaining O_2^-, this would have been clear proof that reaction (2) is a powerful chain-propagation reaction. The absence of this peroxide decomposition is not proof that the reaction does not occur but has significance when related to other experimental results. With the exception of the photochemical decomposition where chain-lengths as high as 2000 have been observed, the maximum chain-lengths reported in reactions with ferrous ions or ozone are very short, about 20 to 30, and the development of a chain is extremely dependent on experimental conditions of mixing and concentration ratios. In other reactions, the decomposition catalysed by ferric ions and by catalase,[20] it is very difficult to account for the observed

[20] George, *Nature*, 1947, 160, 41; *Biochem. J.* (in press). Chance, *Acta Chem. Scandinavica*, 1947, 1, 236 (and further papers in press).

kinetics by the chain process. Thus in deciding on a reaction mechanism the problem is not whether reaction (2) can occur but whether it carries the main burden of the oxygen evolution. The experiments with KO_2 indicate that reaction (2) is not very efficient and so alternative reactions could easily take over the oxygen evolution.

In the actual reaction of KO_2 in aqueous solutions, Dainton and Agar suggest that the HO_2^- ions formed escape by diffusion into the bulk of the solution and that this in part accounts for the fact that no reaction is observable between the peroxide formed from KO_2 and K_2O_2 and any unreacted O_2^-. The experiments in which KO_2 reacts with ferric ions, ferrous ions and catalase show that the peroxide formed *in situ* does react extremely rapidly with these ions *before* diffusion can occur. Furthermore whilst the ferric ions and catalase could react with HO_2^-, it is very difficult to imagine any reaction of ferrous ions as such or modified by the temporarily alkaline environment, reacting with HO_2^- and leading to oxygen evolution. Experimentally 37·5 % of the peroxide formed *in situ* is decomposed into molecular oxygen. For this reason it is very probable that H_2O_2 itself is formed rapidly in the region of the KO_2 particle. So diffusion effects and the peroxide being present as the anion, do not offer satisfactory explanations for the absence of the decomposition of the peroxide formed *in situ* by remaining O_2^-.

Further experiments to check this have been carried out by putting KO_2 into 85 % and 96·5 % H_2O_2 and measuring the O_2 evolution. The results are given in the table. With water alone the KO_2 sample evolves

Run Number.	Solution.	Mg. KO_2 Sample.	Ml. O_2 at N.T.P.	Ml. O_2 per mg. KO_2 sample.
32	85 % H_2O_2	15·0	1·39	0·093
33	85 % H_2O_2	20·0	2·20	0·110
34	96·5 % H_2O_2	5·5	0·50	0·091
35	96·5 % H_2O_2	12·0	1·41	0·117

between 0·086 and 0·109 ml. O_2 per mg. The slight increase observed in runs 33 and 35 is not significant. It is apparently a thermal effect, for on adding KOH to these concentrated peroxide solutions an oxygen evolution of up to 0·012 ml. O_2 per mg. KOH can be obtained. It is very striking that with this very concentrated hydrogen peroxide no more oxygen is evolved than is observed with water alone. In 85 % and 96·5 % H_2O_2, the ratio of peroxide molecules to water molecules is 3 : 1 and 14·5 : 1 respectively, and there can be no doubt that actual collisions between O_2^- in the KO_2 lattice and H_2O_2 molecules are occurring. Nevertheless it is apparent that proton transfer occurs (reaction (3)) rather than electron transfer (reaction (4)).

$$[O_2^- . O_2^-] + H_2O_2 \rightarrow O_2^- . O_2H\cdot + HO_2^- \quad . \quad . \quad . \quad (3)$$

$$[O_2^- . O_2^-] + H_2O_2 \rightarrow O_2^- + O_2 + OH^- + OH^\bullet \quad . \quad . \quad (4)$$

Whether or not the HO_2 radical can react more efficiently with H_2O_2 than does O_2^- awaits experimental confirmation. The fact that an HO_2 radical formed in reaction (3) prefers to react with O_2^- rather than with H_2O_2 in a second collision is some indication that there is little difference in reactivity. Haber and Weiss [31] first chose the HO_2 radical and subsequently Weiss [32] has favoured O_2^-. Dainton and Agar from photochemical evidence prefer the HO_2 radical, although the fact that the photochemical decomposition is inhibited by alkali does not necessarily mean that the

[31] Haber and Weiss, *Proc. Roy. Soc. A*, 1934, 147, 332.

[32] Weiss, *Trans. Faraday Soc.*, 1935, 31, 1547.

chain propagation is less efficient. The photochemical decomposition of hydrogen peroxide is in many ways a special case, for here the chain propagation may well involve excited HO_2 or O_2^- radicals.

Dainton and Agar clearly agree that reaction (2) does not occur in the reaction of KO_2 with water and aqueous solutions of ferric ions, ferrous ions and catalase for they suggest that few O_2^-, H_2O_2 collisions are responsible. This point has been answered above. The abandonment of reaction (2) in the homogeneous reactions of H_2O_2 and Fe^{2+} and Fe^{3+} was not proposed, merely that an alternative "rapid reaction evolving oxygen must be taken into account especially if there is no kinetic evidence for a chain mechanism as in the ferric ion-catalysed decomposition". Catalase decomposes hydrogen peroxide in homogeneous solution at a rate comparable to the decomposition rate of the peroxide formed *in situ* from KO_2 and K_2O_2: the conclusion that reaction (2) is not responsible for the oxygen evolution in homogeneous solution seems completely justified. The kinetics support this conclusion.[1]

In their paper on the reaction between hydrogen peroxide and ozone Taube and Bray [33] state, "HO" reacts with ozone, hydrogen peroxide and the inhibitors (including nitrate ion, sulphate ion and probably perchlorate ion). Of these substances ozone is the only one that must be assumed to react appreciably with HO_2." In their proposed reaction mechanism they did *not* use the reaction between O_2^- or HO_2 and H_2O_2, for their maximum consumption ratios $\frac{\Delta O_3}{[H_2O_2]}$ were unity. Weiss states that at higher concentration ratios $\frac{[O_3]}{[H_2O_2]}$ consumption ratios up to 20 have been observed. The reaction (2) may well occur in these cases but it emphasises the view originally put forward by Haber and Weiss [2] that the transition from consecutive radical reactions to chain reactions may need only a slight change in the balance of competing reactions. The short chain-lengths here emphasise the conclusion that reaction (2) is not a powerful chain-propagation reaction.

Dr. A. Bernanose, Mlle. Thérèse Bremer and Dr. P. Goldfinger (*Brussells* and *Nancy*) (*communicated*): It is well known that Haber and his school were the first to introduce systematically the concept of free radicals such as SO_3H, OH, O_2H, RCHOH, etc., in the kinetics of reactions in solutions. In the course of that work it was shown, more than 15 years ago,[34] that an inhibitor of a free-radical reaction must itself pass into a free radical with a certain stability, as has been explained so clearly by Prof. Melville in his general introduction.[35] We have used the same idea again in a recent research [36] in which we have shown that phthalic hydrazide and 3-amino-phthalic-hydrazide (Luminol) are inhibitors of the hydroperoxide decomposition; the well-known chemiluminescence, which accompanies the reactions of these substances is, without doubt, connected with the inhibition process. By these experiments, as well as by a set of "reduction-activation" [37] experiments we have confirmed the suggestion of Weiss [38] according to whom chemiluminescence is frequently connected with free-radical reactions.

It may be useful to call attention to the fact, that according to this hypothesis the quantum yield per mole of added oxidising agent, which have been hitherto calculated, especially for H_2O_2,[39] should be considerably

[33] Taube and Bray, *J. Amer. Chem. Soc.*, 1940, **62**, 3357.
[34] Goldfinger and Graf v. Schweinitz, *Z. physik. Chem. B*, 1933, **22**, 241, 248.
[35] This Discussion, p. 1.
[36] *Bull. Soc. Chim. Belg.* (in press).
[37] Bacon, *Trans. Faraday Soc.*, 1946, **42**, 140; Baxendale, Evans and Park, *ibid.*, **42**, 155; Morgan, **42**, 169.
[38] Weiss, *ibid.*, 1939, **35**, 219.
[39] Harris and Parker, *J. Amer. Chem. Soc.*, 1935, **57**, 1939.

too low. We are preparing new measurements, and hope to be able, by using the fact that the human eye is sensitive already to a few quanta [40] to determine stationary radical concentrations, which are considerably lower than those measured hitherto. This could be an approach to a type of measurements which Prof. Melville [41] has justly pointed out as being of primary importance.

Prof. M. G. Evans and Dr. J. H. Baxendale (*Leeds*) (*communicated*): We are very interested in the communication by Bernanose, Bremer and Goldfinger. We, too, have used the reaction between OH radicals and Luminol as a method of detecting the presence of OH radicals in a number of electron-transfer reactions, such as the reaction between hydrogen peroxide and ferrous ions and between cobaltic ions and hydroxyl ions. Unfortunately the method is limited in its scope because Luminol, reacting only in its ionised form, can only be used for reactions in alkaline solutions, whereas a number of reactions in which we are interested take place in their simplest form in acid solution.

[40] E.g. Stiles, *Proc. Physic. Soc.*, 1944, **56**, 329.
[41] This Discussion, p. 1.

B.—HYDROCARBONS IN SOLUTION.

THE PHOTOLYSIS AND PHOTO-OXIDATION OF ORGANIC IODIDES IN THE LIQUID STATE.

BY E. OLAERTS AND J. C. JUNGERS.

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Organic iodides undergo, under the influence of ultra-violet light, a decomposition which is interpreted as the splitting of the molecule into an iodine atom and a radical. This method thus constitutes an easy means of producing various radicals and studying their chemical behaviour under comparable conditions. Several iodides have already been studied and values for the quantum yield of some of them have been reported. The results for the photolysis of iodides in different states (gaseous, liquid, dissolved) and by light of various wavelengths are not directly comparable and disagreement exists even for reactions studied under apparently similar conditions. This study refers to the photolysis of several iodides by light of 3150-3000 A. in the liquid state at normal temperature in absence and presence of oxygen.

Experimental.

Preliminary.—Various experiments were carried out with a view to determining the appropriate operating conditions. In Pyrex vessels, transparent to light down to a wave-length of 3000 A., the rate of photolysis gradually decreases as the reaction proceeds. This effect has already been reported by Emschwiller [1] and ascribed to the iodine liberated which acts as an inner filter. When the light is filtered through a nickel chloride solution (3150-3000 A.) the amount of iodine produced varies linearly with the time. The straight line so obtained for iodides not freed from air, does not, however, pass through the origin; the effect is ascribed to the presence of dissolved oxygen. Oxygen has a marked positive effect on the rate of reaction; its presence could not be entirely eliminated by flushing with an inert gas, by pumping off part of the liquid or by distilling it *in vacuo*; the method adopted by Norton [2] of boiling the iodide in a strean of oxygen-free nitrogen proved satisfactory.

[1] Emschwiller, *Ann. Chim.*, 1932, **17**, 413.
[2] Norton, *J. Amer. Chem. Soc.*, 1934, **56**, 2294.

I. Photolysis of Oxygen-free Iodides.

Experimental.—The reactions reported in this section were carried out in conditions similar to those chosen by Norton [2] The reaction cell was a cylindrical quartz vessel (length, 2·6 cm.; diam, 1·7 cm.) with plane windows and an admission tubing which could be sealed off. The filter used to select the 3150 and 3000 A. lines of the mercury spectrum was a layer (1 cm.) of an auramine solution (125 mg./l.). Absorption measurements showed that a layer of a few mm. of liquid iodide are sufficient to absorb entirely the light transmitted by the filter. The sources of light used in these experiments were 75 w.-" Philora " lamps constituted by a small mercury arc, enclosed in a bulb of Uviol glass, operating at high temperature and on 220 V. A.C. The light admitted to the cell was determined by an uranyl oxalate actinometer (quantum yield 0·57 for 3150 A.).[3]

The light received by the cell from one arc was found, in four different experiments, to be 4·3, 4·5, 4·3 and 4·45 × 10^{-6} einstein/hr.; the second lamp gave 2·04, 2·18, 2·15 × 10^{-6} einstein/hr. The intensity of the lamps was checked from time to time and was found to remain fairly constant. The iodine liberated by the decomposition of the iodides was determined by adding a given amount of a $Na_2S_2O_3$ solution (N./200) and titrating the excess with an iodine solution (N./200).

Results.

The values found for the quantum yields of various iodides are presented in Table I.

TABLE I.

Expt.	Time of Irradiation.	G.-atom Iodine Produced × 10^6.	Einstein Absorbed × 10^6.	Quantum Yield.
		I. C_2H_5I		
6	6	8·13	26·34	0·309
7	16	21·1	70·2	0·305
13	6	9·02	26·34	0·340
				av. ~ 0·32
		II. C_3H_7I		
17	6·5	2·92	13·8	0·21
16	9	8·75	39·5	0·22
				av. ~ 0·21
		III. C_4H_9I		
14	7	2·85	30·75	0·093
15	11·65	6	51·2	0·117
				av. ~ 0·100
		IV. $C_5H_{11}I$		
8	13	4·22	57	0·074
9	18·66	4·7	82	0·058
10	29·5	8·15	129·4	0·063
				av. ~ 0·065
		V. *Iso*-C_3H_7I		
22	4	7·3	8·49	0·86
23	4	6	8·49	0·71
25	8	12·75	16·95	0·75
				av. ~ 0·77
		VI. C_6H_5I		
11	20·6	3·28	90	0·036
12	21·5	2·92	94·5	0·031
				av. ~ 0·033

[3] Forbes and Heidt, *J. Amer. Chem. Soc.*, 1934, 56, 2363.

The normal alkyl iodides show a regular decrease in quantum yield with increasing length of the carbon chain; the value for *iso*propyl iodide is markedly higher than for the corresponding normal iodide; the value for phenyl iodide is slightly lower than might be expected from its molecular weight and this is probably related to the different nature of its bonds.

The photolysis of amyl iodide has been further studied by Lontie [4] who, by determining the iodine produced with a photometer, could follow the reaction continuously from the start. This does not, however, constitute an independent check as the light intensity was still measured by the uranyl-oxalate actinometer. The results of Lontie agree with those presented in this paper and confirm that the variations observed in the yield are due mainly to the incomplete removal of oxygen and slight variations in temperature; this reaction, contrary to what Norton observed for ethyl iodide, and in accord with the results of other authors, gives a definite temperature coefficient under these conditions.

The quantum yields were measured mainly with a view to determining the relative rates of reaction of the different iodides. The result obtained for ethyl iodide is, however, in surprisingly good agreement with the value determined by Norton (0·315) under similar conditions. These results are on the other hand markedly lower than the ones reported by Iredale [5] (1 and 1·2 for 3650 and 3000 A. resp.) and by Emschwiller [1] (1 for 3650 A.). The presence of oxygen is insufficient to account for the high yields as they are even higher than those obtained in this research for iodide saturated with oxygen under atmospheric pressure.

The value of 2·5 found by Emschwiller for the quantum yield of butyl iodide at 90° C. and the higher value for ethyl iodide indicated by extrapolation from values at lower temperatures would point to a chain mechanism; the best evidence available is not, however, in agreement with this suggestion.

II. Photolysis of the Iodides Saturated with Oxygen.

Experimental.—As the oxygen is used up during the decomposition of the iodide, precautions must be taken to keep the liquid saturated. The reaction cells used for this purpose were made of Pyrex tubing (22 cm. length; 0·9 cm. diam.) sealed to a vessel (15 cm. length; 5 cm. diam.) which serves as oxygen

TABLE II.

Run.	Iodide.	Pressure of Oxygen in cm.	G.-atom Iodine Produced × 10^6.	Einstein Absorbed × 10^6.	Quantum Yield.
		A. Influence of oxygen pressure.			
1	C_4H_9I	1	18·9	59	0·32
1	—	25	21·8	59	0·37
2	—	25	14·85	38·3	0·38
1	—	50	23·45	59	0·4
1	—	75	26	59	0·44
2	—	75	16·55	38·3	0·43
3	C_6H_5I	5	14·3	46	0·31
3	—	15	14·7	46	0·32
3	—	35	15·3	46	0·33
3	—	70	16·9	46	0·37
		B. Nature of the iodide.			
5	C_2H_5I	65	23	43·6	0·53
9	C_3H_7I	65	16·7	35	0·48
1	C_4H_9I	65	extrapolated		0·42
9	$C_5H_{11}I$	65	13·4	35	0·38
8	C_6H_5I	65	15	43·6	0·34

reservoir; the cell was surrounded by a Pyrex jacket (2·1 cm. wide) and the annular space filled with a filter solution (200 mg. K_2CrO_4/l.). Four cells of this kind were mounted on a support and were tilted every minute so that the liquid could spread in the reservoir and remain saturated with oxygen. A fifth cell filled with uranyl-oxalate solution served as a test of the intensity of the

[4] Unpublished data. [5] Iredale, *J. Physic. Chem.*, 1929, 33, 290.

absorbed light. The light source in these experiments was a Heraeus mercury arc operated on 80 v. D.C. and 3·5 amp. Errors due to reflection or incomplete absorption might be expected to be important in this set-up, but measurements on oxygen-free ethyl and butyl iodide gave quantum yields in fair agreement with those determined in the quartz cell.

Results.—The quantum yields for the photolysis of various iodides under given oxygen pressures are presented in Table II. The results (A) show quite clearly that the yields remain markedly higher than for the pure iodides (3 times for butyl and 9 times for phenyl iodide) down to very low oxygen pressures. This agrees with the observation made several times on the influence of even small traces of oxygen.

In (B) the quantum yields are given for various iodides under the same oxygen pressure. They show a difference with the nature of the iodide, which is definitely smaller than for the oxygen-free substances.

Discussion.

The small yields observed for the iodides as compared to that of hydrogen iodide, are accounted for by the recombination of the radical with the iodine resulting from the primary process :

$$RCH_2I + h\nu = RCH_2 + I \qquad (1)$$
$$RCH_2 + I = RCH_2I \qquad (2)$$
$$RCH_2 + I_2 = RCH_2I + I. \qquad (2')$$

Radicals from other sources have indeed been shown to yield the corresponding iodide with iodine.[6] The reaction of the radical with molecular iodine seems to play no important role in the liquid-phase photolysis as shown by the independence of the yield of iodine produced in the reaction.

The alkyl radicals escaping recombination would react with an iodide molecule to give a paraffin and a radical which would eventually decompose into an olefin and iodine :

$$RCH_2 + RCH_2I = RCH_3 + RCHI \qquad (3)$$
$$RCHI = RCH + I. \qquad (4)$$

The iodine atoms associate in a triple collision to molecular iodine :

$$I + I + (M) = I_2 + (M). \qquad (5)$$

The association of two radicals is considered highly improbable as reaction (2) keeps the radical concentration low and the steric factor[7] is only 10^{-4} to 10^{-5}. This conclusion is supported by the results of the chemical analysis which reveals only insignificant traces of the resulting hydrocarbon, $(RCH_2)_2$.

The breaking-up of heavier radicals is only slightly probable as the paraffin and the corresponding olefin are generally formed in equal quantities ; for complex radicals, e.g. *tert.*-butyl, such a mechanism might, however, play an important role.[1]

According to this scheme the quantum yield would be governed by an expression of the kind :

$$Q.Y. = \frac{2k_3[RCH_2I]}{k_2[I] + k_3[RCH_2I]}.$$

If one substitutes for the atomic iodine concentration, it appears that the quantum yield should rise with the concentration of the iodide, the total pressure and the temperature and diminish with increasing light intensity.

For pure iodides in the gas phase the yields are known to be very small. This can qualitatively be accounted for since reaction (2) proceeds without activation energy and with a steric factor close to unity, while reaction (3), assuming an activation energy of 10 kcal., would be efficient only once in 10^7, or even less, according to the value of the steric factor. The balance between reaction (2) and (3), and thus the quantum yield can, however, be modified in different manners.

[6] Gorin, *J. Chem. Physics*, 1939, **7**, 286.
[7] Bawn, *Trans. Faraday Soc.*, 1935, **31**, 1542.

By adding a high concentration of a chemically inert gas (CO_2, or A) the recombination of iodine atoms is favoured; the corresponding radicals are thus compelled to react according to (3). West and Schlessinger have increased the reaction rate of ethyl iodide very markedly in this way.[8]

The reaction can also be favoured by combining the iodine with mercury or silver. The radical concentration can be raised so that reaction (3) is strongly favoured and even the association of radicals becomes effective; methyl iodide gives considerable quantities of ethane, apparently due to the combination of methyl radicals, while for ethyl iodide the composition of the products is not markedly modified; no butane, characteristic of ethyl radical combination, is reported.[8] This difference in behaviour is of great significance and points to a difference in strength of the C—H bond in the iodides. If the reaction $CH_3 + CH_3I$ is difficult, the association of radicals to ethane will be favoured.

By elimination of radicals the reaction can also be favoured. If hydrogen iodide is added to gaseous methyl iodide, the quantum yield, normally very low ($\sim 0{\cdot}02$), is raised to about unity with 5 %, and to 2 with 40 % or more HI added.[9] Methyl radicals can then react according to:

$$CH_3 + HI = CH_4 + I.$$

In the presence of hydrogen iodide, liquid ethyl iodide decomposes into ethane.

Oxygen also is very efficient in removing radicals. The value of 2, first reported for the quantum yield of the photo-oxidation of methyl iodide,[10] has been corrected to 1 and the mechanism proposed to account for it is:[11]

$$RCH_2 + O_2 = RCH_2O_2 \quad . \quad . \quad . \quad . \quad (6)$$
$$RCH_2O_2 + RCH_2 = RCH_2OH + RCHO \quad . \quad . \quad (7)$$

where R = H. This mechanism could be extended to higher iodides as the corresponding aldehydes have been identified in the products.[1]

Nitric oxide which inhibits chain reactions has a positive influence on the photolysis of methyl iodide which is ascribed to the reaction:[12]

$$CH_3 + NO = CH_3NO.$$

In the liquid phase, where the probability of combination of iodine atoms is higher and where the relative concentration of iodide to atomic iodine is much greater than in the gas phase, the reaction proceeds more rapidly. There is, however, a great difference in behaviour between the various iodides. To account for this, a steric factor can be first considered; such a factor has been invoked to account for the different rate of polymerisation of unsaturated hydrocarbons photosensitised by isomeric organic iodides.[13] In the photolysis, a steric factor would be operative in reaction (2) as well as (3). This factor is, however, unable to account for all the differences noticed between the different iodides. To start with, hydrogen iodide has a quantum yield of 2; that of methyl iodide is very small in the liquid phase and in solution, as well as in the gas phase; the yield is higher again for liquid ethyl iodide but diminishes with the molecular weight for normal iodides; finally, there is a marked difference between isomeric iodides. This suggests that the reactivity of the hydrogen in the iodide molecule has to be taken into account in reaction (3). Such a difference between aromatic, primary, secondary and tertiary hydrogen is found towards various reagents.

[8] West and Schlessinger, *J. Amer. Chem. Soc.*, 1938, **60**, 961.
[9] Iredale and Stephan, *Trans. Faraday Soc.*, 1931, **27**, 468.
[10] Bates and Spence, *J. Amer. Chem. Soc.*, 1931, **53**, 1689.
[11] Blaedel, Ogg and Leighton, *ibid.*, 1942, **64**, 2500.
[12] Iredale and McCartney, *ibid.*, 1946, **68**, 144.
[13] Jungers and Yeddanapalli, *Trans. Faraday Soc.*, 1940, **36**, 483.

Further the quantum yield has been shown to increase with decreasing wavelength of the light;[9, 14] this effect has been observed for other photodecompositions and has been explained by assuming that the energy in excess of the bond to be broken appears as recoil energy. The lighter radicals would be expelled more violently; they would thus have less chance of recombining and might even be more effective in their collision with an iodide molecule: both effects favour decomposition. Heavier particles would be less energetic and the statistical distribution might not be established.

The oxidation is a very efficient process; while in the gas phase the quantum yield is 1, it does not reach this value in liquid iodides. More striking is the fact that while small traces of oxygen have a very marked effect, increasing the pressure several hundred times (and thus the concentration of oxygen in the liquid *if* Henry's law holds) modifies the yield to a relatively small extent.

According to (1), (2), (3), the quantum yield would be governed by an expression of the form:

$$\text{Q.Y.} = \frac{2k_3[\text{RCH}_2\text{I}] + 2k_6[\text{O}_2]}{k_2[\text{I}] + k_3[\text{RCH}_2\text{I}] + 2k_6[\text{O}_2]}.$$

If we consider higher iodides or methyl iodide, reaction (3) is negligible compared to (2) and (6) and the expression reduces to:

$$\text{Q.Y.} = \frac{2k_6[\text{O}_2]}{k_2[\text{I}] + 2k_6[\text{O}_2]}.$$

There is no appropriate test available for this expression. The fact that the iodides which show the smallest quantum yield in photolysis are also less easily oxidised might lead one to believe that the products do not reach statistical distribution and that a fraction of radicals escape oxidation in this way.

The quantum yields in solution are, as expected, higher than in the gas phase and of the same order of magnitude as for the liquid iodides. This might be due to the factors which are operative in the pure liquids, in particular, a more active recombination of iodine atoms.

There are, however, striking differences which are difficult to explain. Gibson and Iredale[15] find for different iodides in benzene a quantum yield close to unity and for *tert.*-butyl iodide, particularly a value markedly higher (1·04 for 3130 A.) than the one reported by Emschwiller for the pure liquid (0·25 for 3650 A.). West and Paul[14] report for the photo-oxidation of a 1·8 M. ethyl iodide solution in hexane a quantum yield of 2, higher than the value for the gas (1) and the pure liquid. These and other discrepancies might be accounted for to some extent by the characteristics of the light used and the higher oxygen concentrations with respect to the iodide. The possibility of a chemical action of the solvent should, however, not be overlooked as it has been shown that radicals react with various hydrocarbons.

At this stage, a mechanism should, in view of the analogy of the primary process in the photolysis of the iodides, be general enough to account, in terms of relative frequency of the secondary reactions, for the differences in behaviour of the various iodides. Although the scheme put forward agrees qualitatively with the bulk of the experimental results, it does not give a satisfactory explanation of all the reported facts. It is only with reliable values for the quantum yield, and further information on the influence of dilution, temperature, intensity and energy of light used, that the proposed mechanism could be safely tested. The study of the influence of foreign substances might be of great help in recognising the factors responsible for the difference in behaviour of the various iodides.

[14] West and Paul, *Trans. Faraday Soc.*, 1932, 28, 688.
[15] Gibson and Iredale, *ibid.*, 1936, 32, 571.

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Summary.

The quantum yield of the photolysis and the photo-oxidation of several liquid iodides by light of 3130-3000 A. have been determined at normal temperature. Some of the factors likely to account for the variation in quantum yield for a given iodide and the differences in yield between different iodides are pointed out.

Résumé.

On a déterminé à température ordinaire le rendement de quantique pour la photolyse et la photo-oxydation de plusieurs iodures liquides par une lumière de 3130-3000 A. On discute les facteurs qui peuvent rendre compte de la variation dans le rendement pour un iodure donné et des différences de rendement entre divers iodures.

Zusammenfassung.

Die Quantenausbeute für die Photolyse und Photo-oxydation von mehreren flüssigen Jodiden im Licht von 3130-3000 A. ist bei gewöhnlichen Temperaturen bestimmt worden. Die Faktoren, die wahrscheinlich die Veränderungen der Ausbeute bei einem gegebenen Jodid und den Unterschied der Ausbeute bei verschiedenen Jodiden verursachen, werden besprochen.

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THE FORMATION AND REACTIONS OF FREE RADICALS IN SOLUTION AT LOW TEMPERATURES.

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The thermal and photochemical dissociation of the metal alkyls has been employed frequently as a source of free radicals. Most of this work has been carried out with the lead and mercury alkyls (PbR_4, HgR_2) in the gas phase. These thermal dissociations require a comparatively high temperature, occur in several stages, and are complicated by interaction between radicals and undissociated or partially dissociated metal alkyls. In searching for a convenient source of radicals suitable for lower temperature thermal investigations, we first examined the lithium alkyls. The lower members are colourless solids, but lithium propyl and butyl are liquids. Attempts to distil these compounds at their melting points (m.p. $LiC_2H_5 \simeq 95°$ c.) resulted in serious decomposition. At temperatures below their melting points their vapour pressures were remarkably low and hardly sufficient for thermal decomposition studies. In solution, however, the alkali alkyl appears to be very stable. Thus, lithium methyl showed no decomposition on long periods of heating in phenetole at 150° c. Our attention was therefore directed towards the unstable silver and copper alkyls. Previous investigations by Gilman and his co-workers [1] and by Semerano and Riccoboni [2] have shown that

[1] Gilman and Woods, *J. Amer. Chem. Soc.*, 1943, 65, 435.
[2] Semerano and Riccoboni, *Ber. B*, 1941, 74, 1089; Semerano and Riccoboni, *Z. physik. Chem. A*, 1941, 189, 203; Semerano, Riccoboni and Callegari, *Ber. B*, 1941, 74, 1297.

solid silver methyl and ethyl in alcohol suspension decomposed at temperatures below 0° c. to give hydrocarbons, which they suggested are formed from free radicals liberated in the dissociation.

In the present work the rate of decomposition of silver methyl in ethyl alcohol solution has been measured in the temperature range, − 50° to − 20° c. The products of the decomposition of silver ethyl and copper methyl have been determined and the nature of the free-radical reactions elucidated.

Experimental.

Silver and copper alkyls were prepared by the reaction of the metal nitrates with lead tetramethyl or tetraethyl in alcoholic media. The apparatus employed is shown in Fig. 1 and the procedure was briefly as follows. 40 cc. of aldehyde-free

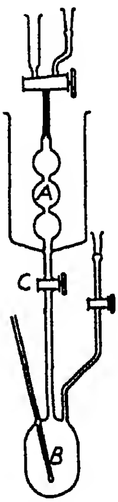

Fig. 1.

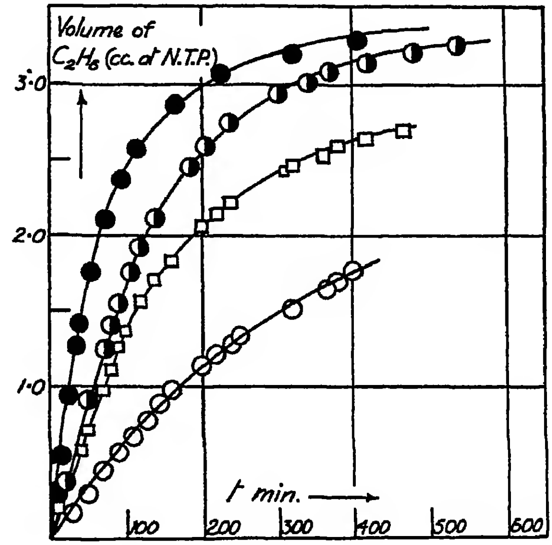

Fig. 2.

alcohol were carefully freed from air by running into the evacuated vessels A and B in 10 cc. amounts, each portion being further degassed by cooling and evacuation. 4 cc. $AgNO_3$ solution (1·2 g./100 cc. alcohol) were then added, degassed and followed by a further 40 cc. alcohol, added in portions as before. 0·25 cc. lead tetramethyl in 15 cc. alcohol was degassed in A. The two solutions in A and B were cooled to the temperature of the experiment before mixing which occurred on opening the tap C. The temperature of the lead tetramethyl solution was ascertained by trial and error so as to give no temperature change on mixing. The rate of decomposition was followed by continuous evacuation of the gases by a Toepler pump into a calibrated gas-tube, the volume of the gases being read at about 5- to 10-min. intervals. The gases were then analysed as previously described.[8]

In all experiments, unless specially noted, the lead alkyl was in excess (5 moles per mole silver nitrate) and the conditions were arranged so that all the silver alkyl formed was in solution. Estimates of the solubility of the silver alkyl in different solvents were made by the preparation of optically-clear solutions and determination of the silver formed on decomposition. The approximate solubilities at − 80° c. are: Silver methyl in (*a*) ethyl alcohol, 0·004 g./10 cc., (*b*) methyl alcohol, 0·003-0·004 g./10 cc., (*c*) amyl alcohol, 0·006 g./10 cc., (*d*) *n*-butyl phthalate and decalin, insoluble. Silver ethyl: solubility in methyl alcohol, 0·03 g./10 cc.

[8] Bawn and Milsted, *Trans. Faraday Soc.*, 1939, 35, 889.

Results and Discussion.

Kinetics of Decomposition of Silver Methyl in Ethyl Alcohol Solution.

At temperatures between − 60° and 0° c. silver methyl in methyl or ethyl alcohol solution decomposed quantitatively to give ethane and silver. The reactions which take place have been shown to be the following:

$$AgCH_3 \rightarrow Ag + CH_3 \quad . \quad . \quad . \quad . \quad (1)$$
$$CH_3 + CH_3 \rightarrow C_2H_6 \quad . \quad . \quad . \quad . \quad (2)$$

Table I gives the material balance at − 10° and − 29° c. in the two alcohols.

TABLE I.

Concn. of $AgCH_3 = 2{\cdot}73 \times 10^{-3}$ moles/l.

Solvent.	Temperature °C.	Carbon Balance Per Cent. $Ag^+ \equiv 1\ CH_3$.
CH_3OH	−10	100·5 } C_2H_6 was the only hydrocarbon
C_2H_5OH	−29	97·1
C_2H_5OH	−10	101·1

This was determined from the amount of $AgNO_3$ used and the quantity of hydrocarbon formed according to eqn. (1) and (2). The plot of the volume of ethane formed as a function of time at a series of temperatures is shown in Fig. 2. The decomposition accurately obeys the first order law,

$$kt = \log_e \frac{V_\infty}{V_\infty - V_t}$$

where V_∞ = volume of ethane formed on complete decomposition and V_t = volume of ethane at time t. This is shown by the plot of $\log_{10} (V_\infty - V_t)$ against t in Fig. 3. This was further confirmed by determination of the time of half-change, which was independent of the initial concentration (Table II). The plot of $\log_{10} k$ against $1/T$ obeys a straight-line relationship (Fig. 4), the slope of which corresponds to an activation energy of 10,500 ± 1,000 cal./mol. The scatter of the points was primarily due to the difficulty of attaining constant-temperature conditions over the initial period of decomposition, following the mixing of the cooled solutions. The rate of decomposition over the whole temperature range of the investigation may be represented by the law:

$$k = 5{\cdot}5 \cdot 10^4 e^{-10{,}500/RT}\ \text{sec.}^{-1}.$$

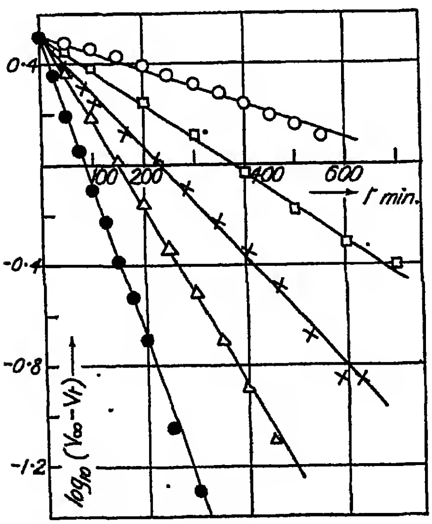

FIG. 3.

Some preliminary observations with silver ethyl in ethyl alcohol at − 40° c. and room temperature showed that the decomposition products consist of a mixture of ethane, ethylene and butane. This indicates an initial decomposition into the free ethyl radical followed by association and disproportionation reactions:

$$AgC_2H_5 \rightarrow Ag + C_2H_5 \quad . \quad . \quad . \quad . \quad (3)$$
$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6 \quad . \quad . \quad . \quad (4)$$
$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

A similar reaction scheme has been proposed by Semerano and Riccoboni [2] for the decomposition of silver ethyl suspended in alcohol and the disproportionation reaction (4) thus appears to have a very low activation energy, in agreement with our previous measurements in the gas phase.[4]

Whilst we regard the above results, namely, the first-order decomposition to give ethane and the disproportionation reaction with silver ethyl, as justifying the assumption of a free-radical mechanism, various other reactions have been investigated in order to support this view, but without any striking success. Oxygen, water, and hydroquinone had no influence on the reaction at temperatures up to − 10° c. and it appears that methyl radicals are unreactive towards these substances at low temperatures. The addition of an excess of an alcoholic solution of iodine to the silver methyl solution at − 30° c., that is, under

TABLE II.

Temp. °C.	Concn. of Silver Methyl (mol./l.)	Time of Half Change (min.)
−35·0	0·00272	75·5
−34·8	0·00204	79·0
−42·3	0·00272	123·0
−42·1	0·00204	127·0

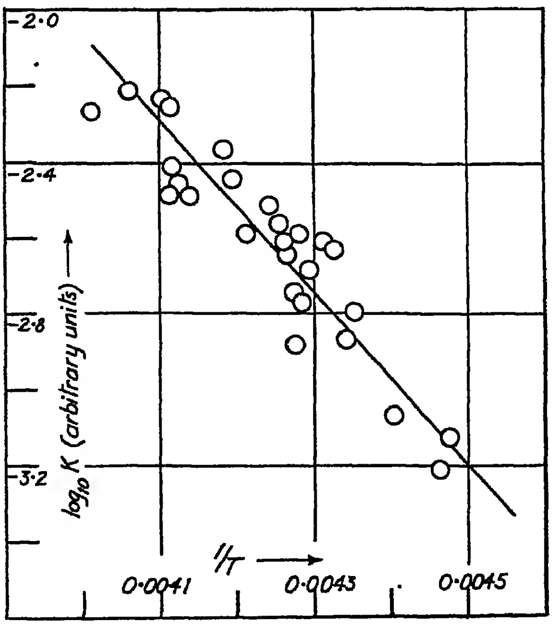

FIG. 4.

conditions when the decomposition is proceeding fairly rapidly, reduced the yield of ethane to between 5 and 12 %. This small amount of ethane was most certainly that formed by normal decomposition before the iodine was added. The gas-phase reaction of methyl radicals with iodine molecules

[4] Bawn and Tipper, this Discussion.

is known to require little or no activation energy and so it is possible that the methyl radicals formed are removed by the reaction [5]

$$CH_3 + I_2 \rightarrow CH_3I + I. \quad . \quad . \quad . \quad . \quad (6)$$

The alternative possibility is that the iodine destroys the silver methyl according to

$$AgCH_3 + I_2 \rightarrow AgI + CH_3I. \quad . \quad . \quad . \quad (7)$$

No definite decision can be reached between these mechanisms but it is quite probable that (7) requires an activation energy and does not occur at $- 30°$ c.

It was also considered possible that the methyl radicals might react with stable radicals of the Gomberg type, since such association reactions would require little activation. The difficulty, however, was to find a radical which was not associated at $- 30°$ c. Hexaphenyl ethane, as anticipated, was too poorly dissociated and had no effect on the reaction. αα-diphenyl-β-trinitrophenyl hydrazyl, which exists as a free radical in solution, reduced the ethane yield by 5 % at 20° c. and at a concentration where a 20 % reduction was expected if all the radical added underwent reaction. A change of colour of the radical was noticed during the reaction. The results, however, are inconclusive.

The Mechanism of Decomposition.

Few data are available on the properties of the silver and copper alkyls in solution, but general considerations would indicate that the carbon-metal bond is largely ionic in character. The corresponding alkali alkyls show strong polar properties. They ionise in zinc diethyl, are very non-volatile and are poorly soluble in organic solvents.[6] Dipole moment

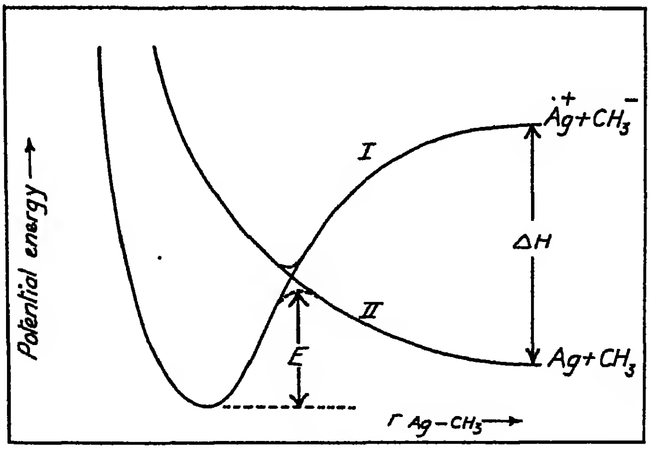

FIG. 5.

measurements on lithium butyl in benzene show that the Li—C bond is about 45 % ionic.[7] Organo-silver and -copper compounds are insoluble, or only slightly soluble, in organic solvents and this suggests a polar structure.

It is reasonable to assume that the structure of silver methyl is predominantly $Ag^+CH_3^-$. The dissociation may be represented in terms of potential energy diagrams in the following manner. Fig. 5, curve 1,

[5] Steacie, *Atomic and Free Radical Reactions*, p. 477.

[6] Hein and Schramm, *Z. physik. Chem. A*, 1930, **151**, 234; Hein, Petzchner, Wagler and Segitz, *Z. anorg. Chem.*, 1924, **141**, 161.

[7] Rogers and Young, *J. Amer. Chem. Soc.*, 1946, **68**, 2748.

shows (qualitatively) the dissociation into ions. The final products experimentally are free methyl and silver, and thus the final energy state will lie lower than the state of dissociation into ions by the energy difference $\Delta H = I_{Ag} - E_{CH_3}$, where E_{CH_3} is the electron affinity of the methyl radical and I_{Ag} is the ionisation potential of silver. $E_{CH_3} = 20$ kcal.[8] $I_{Ag} = 175$ kcal. Therefore $\Delta H = 155$ kcal./mol. Curve II shows the potential energy for the homopolar interaction between Ag and CH_3. It is not certain whether or not the curve actually has a minimum corresponding to a stable homopolar state, but the main point is that interaction is slight. The relative positions of the curves is uncertain and may be modified by solvation effects. In the separated condition the radicals are more stable than the ions, but when combined the ionic state is more stable than the homopolar form. The potential energy curves must therefore "cross," as shown in Fig. 5. There is no actual crossing, as the curves separate, as indicated by the dotted lines, giving two potential energy surfaces. The lower one represents the actual path of the reaction to give radicals. The activation energy is given by the height of the crossing point E and the rate is given by this value and the frequency factor A. In a normal first-order reaction A is equal to about 10^{13} and the low experimental value of $5 \cdot 5 \times 10^3$ indicates a very high restriction at the crossing point. This would be so if there were a small interaction, and thus little separation of the curves at the crossing point.

Formation and Decomposition of Copper Methyl.

I. Reaction in Ethyl Alcohol.—The reaction between cupric ion and lead tetramethyl in ethyl alcohol follows a markedly different course from that of the silver-ion reaction. Whereas in the latter case ethane was the sole gaseous reaction product, with cupric ion the gases formed contain large amounts of methane in addition to ethane. The material balance, based on the $CH_4 + C_2H_6$ formed, showed that the equivalent of two methyl groups was formed for each

TABLE III.

REACTION BETWEEN Cu^{++} AND $Pb(CH_3)_4$ IN ETHYL ALCOHOL.

Temp. °C.	Experimental Conditions.	Initial Cu^{++} concn. g. mol./l.	CH_4 cc. N.T.P.	C_2H_6 cc. N.T.P.	Ratio C_2H_6/CH_4.	Carbon Balance, % ($Cu^{++} \equiv 2CH_3$).
16·0	$Cu(NO_3)_2 . 3H_2O$; 4·8% aq. C_2H_5OH	$2 \cdot 55 \times 10^{-3}$	5·38	2·48	0·46	87·1
14·5	$Cu(NO_3)_2 . 3H_2O$; 20 % aq. C_2H_5OH	$2 \cdot 55 \times 10^{-3}$	5·81	3·37	0·58	105·5
16·0	$Cu(NO_3)_2 . 3H_2O$; distilled C_2H_5OH	$2 \cdot 55 \times 10^{-3}$	4·78	2·56	0·53	83·3
15·0	$Cu(NO_3)_2 . 3H_2O$; distilled C_2H_5OH	$2 \cdot 55 \times 10^{-3}$	5·54	3·14	0·57	92·9
8·2	$Cu(NO_3)_2 . 3H_2O$; very dry alcohol	$2 \cdot 55 \times 10^{-3}$	6·34	2·96	0·47	103·0
18·0	$Cu(NO_3)_2$ (anhyd.) ; very dry alcohol	$1 \cdot 03 \times 10^{-3}$	2·45	1·15	0·47	99·0

Cu^{++} ion consumed in ethyl alcohol solution. The ratio of ethane/methane by volume was 0·5, that is, two molecules of methane to one of ethane are formed. The results are summarised in Table III. In each experiment the lead tetramethyl was present in large excess.

The variation of the material yield from 100 % in the above and subsequent results is due essentially to the fact that the yield is calculated on the concentration of cupric ion used initially and weighed as $Cu(NO_3)_2 . 3H_2O$. We have evidence that $Cu(NO_3)_2 . 3H_2O$, dried in a desiccator, loses moisture, and

[8] Baughan, Evans and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377.

it was difficult to ensure that the exact degree of hydration was three. It is seen from these results that water had no material effect on the yield or the ratio C_2H_6/CH_4.

Detailed investigation showed that the reaction occurs in two well-defined and independent stages, the first of which produces ethane and the second, methane. The analysis of the results shows that these reactions are:

STAGE 1. $Cu^{++} + Pb(CH_3)_4 \rightarrow Cu^{+} + Pb(CH_3)_3^{+} + CH_3$ . . (8)

$CH_3 + CH_3 \rightarrow C_2H_6$ . . . . . . (9)

STAGE 2. $Cu^{+} + Pb(CH_3)_4 \rightarrow CuCH_3 + Pb(CH_3)_3^{+}$ . . (10)

$CuCH_3 + \text{solvent} \rightarrow CH_4$ . . . . . (11)

The justification for this subdivision is found in the following observations. (*a*) When the reaction (using an excess of lead tetramethyl) was carried out at $-45°$ c., the gaseous product was ethane and a primrose precipitate of copper methyl was deposited. On warming the solution to room temperature, methane was evolved with the formation of a brownish precipitate. The results of the two-stage reaction are summarised in Table IV.

TABLE IV.—Cu^{++} ION-LEAD TETRAMETHYL REACTION IN ETHYL ALCOHOL.

Temperature °c.		Concn. of $Cu(NO_3)_2 . 3H_2O$ (g. mol./l.)	CH_4 cc. N.T.P.	C_2H_6 cc. N.T.P.	Ratio C_2H_6/CH_4.	Carbon Balance. % ($Cu^{++} \equiv 2CH_3$).
Stage 1.	Stage 2.					
−40		2·55 . 10⁻³	0·0	1·912	0·46	110·0
	+20		6·83	1·237		
−35		2·55 . 10⁻³	0·32	3·04	0·50	110·6
	+20		6·23	0·26		
−3·0		2·55 . 10⁻³	4·08	3·01	0·59	100·8
	+20		1·42	0·24		

(*b*) If a large excess of Cu^{++} ion were employed, then this would be expected, on the above mechanism, to remove rapidly all the lead tetramethyl by reaction (8), and thus the reaction of the cuprous ion according to (10) would be inhibited. This was the result observed with a threefold excess of cupric ion ($[Cu^{++}] = 1{\cdot}28 \times 10^{-2}$ mol./l.). The gas evolved consisted of 96·7 % ethane and 3·3 % methane by volume. No copper methyl was precipitated and the solution retained the characteristic colour of the Cu^{++} ion.

(*c*) A further confirmation of the proposed mechanism was provided by the observed production of cuprous ion (indicated by an acetone solution of *p*-dimethylaminobenzal rhodanine) when excess Cu^{++} was used and reaction (10) inhibited.

II. Reaction in Methyl Alcohol.—In methyl alcohol more hydrocarbon was formed per Cu^{++} consumed than in ethyl alcohol. The carbon balance showed that the equivalent of three methyl groups were liberated for each Cu^{++} ion used up and the volume ratio of the gases was now $4CH_4/1C_2H_6$. The reaction, as in ethyl alcohol, was separable into two stages. At $-45°$ c. copper methyl was precipitated and ethane only was evolved. On warming to room temperature methane was liberated. The difference in behaviour in the two solvents is revealed by the amount of methane produced in the second stage of the reaction. The results are summarised in Table V.

Discussion.

The decomposition and reactions of copper methyl differ in many respects from the corresponding reactions of silver methyl. It is clear that the decomposition reaction is not simply the formation of methyl radicals and metallic copper, for ethane would then have been the gaseous product. Neither can it be assumed that the methyl radicals react with

the solvent at room temperature to produce methane, because this reaction does not occur when silver methyl is decomposed at room temperature. The formation of methane, namely two molecules in ethyl alcohol and four in methyl alcohol for each ethane molecule (or according to eqn. (10) for every two copper methyl molecules formed), may be best explained by assuming direct reaction of $CuCH_3$ with the solvent. For example :

$$CuCH_3 + C_2H_5OH \rightarrow Cu + CH_4 + C_2H_5O \qquad (12)$$
$$C_2H_5O + C_2H_5O \rightarrow C_2H_5OH + CH_3CHO. \qquad (13)$$

TABLE V.—REACTION BETWEEN Cu^{++} ION AND $Pb(CH_3)_4$ IN METHYL ALCOHOL.

Temperature °C. Stage 1.	Temperature °C. Stage 2.	Concn. of $Cu(NO_3)_2 . 3H_2O$ (g. mol./l.)	CH_4 cc. N.T.P.	C_2H_6 cc. N.T.P.	Ratio C_2H_6/CH_4.	Carbon Balance. % ($Cu^{++} \equiv 3CH_3$)
18		$2 \cdot 55 . 10^{-3}$	13·15	3·45	0·26	112·5
18		$2 \cdot 55 . 10^{-3}$	12·58	3·15	0·25	105·9
−45		$1 \cdot 91 . 10^{-3}$	0·0	2·14	0·27	107·0
	+18		9·25	0·40		
−40		$1 \cdot 91 . 10^{-3}$	0·0	2·24	0·29	114·5
	+20		9·66	0·61		

In methyl alcohol, an additional molecule of methane is formed from the alcohol. The mechanism of this reaction is not yet clear.

Initiation of Polymerisation.—It was observed that when lead tetramethyl or ethyl was added to an alcoholic solution of styrene, methyl methacrylate or acrylonitrile containing cupric nitrate, polymerisation of the monomers occurs rapidly at room temperature. Cupric ions or the lead alkyl alone did not initiate polymerisation and, moreover, the presence of the monomer inhibited the formation of copper methyl (or ethyl). In contrast to these observations, the reaction of $AgNO_3$ with lead tetra methyl (or ethyl) did not initiate polymerisation. Neither was the decomposition of the silver methyl at 0° c. or lower, effective in this respect. It appears, therefore, that the polymerisation initiator is not the free alkyl radical but that initiation is most probably determined by an oxidation-reduction reaction involving the copper ions.

One of us (F. J. W.) is indebted to the Distillers Co. Ltd., for a Research Grant.

Summary.

Silver methyl and ethyl have been prepared by the reaction of $AgNO_3$ and lead tetra methyl (or tetra ethyl) in alcoholic solution. In the temperature range − 60° to − 20° c., $AgCH_3$ decomposed according to the first-order law, $k = 5 \cdot 5 \; 10^5 \, e^{-10,600/RT}$. The low temperature-independent factor is explained in terms of the potential energy surfaces for the reaction $Ag-CH_3 \longrightarrow Ag + CH_3$. The methyl radicals liberated combine quantitatively to form ethane but with ethyl radicals the disproportionation reaction

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6$$

also occurs.

The corresponding reaction between cupric compounds and the lead alkyls follows a different course and the probable mechanism of the reaction is :

$$Cu^{++} + Pb(CH_3)_4 \rightarrow Cu^{+} + Pb(CH_3)_3^{+} + CH_3$$
$$Cu^{+} + Pb(CH_3)_4 \rightarrow CuCH_3 + Pb(CH_3)_3^{+}.$$

The copper methyl does not decompose to give methyl radicals, but reacts with the solvent to form methane.

The combination of Cu^{++} ion with lead tetra-methyl or -ethyl is a powerful polymerisation catalyst and the chain initiation is not a consequence of the formation of the free alkyl radicals.

Résumé.

On a préparé l'argent-méthyl et l'argent-éthyle. Le premier se décompose entre —60 et —20° c. d'après une loi du premier ordre: $k = 5{\cdot}5 \times 10^{-5} e^{-10{,}500/RT}$. On explique le faible facteur indépendant de la température par les surfaces d'énergie potentielle pour la réaction: $Ag^+CH_3^- \rightarrow Ag + CH_3$. La réaction correspondante entre les composés cuivriques et les plomb-alcoyles suit un cours différent et l'on suggère un mécanisme probable. La combinaison d'ions Cu^{++} avec le plomb-tétra-méthyle ou éthyle est un catalyseur puissant de polymérisation et l'initiation de chaîne n'est pas une conséquence de la formation de radicaux libres alcoyles.

Zusammenfassung.

Silbermethyl und -äthyl sind dargestellt worden; das erstere zersetzt sich zwischen $-60°$ und $-20°$ c. als Reaktion erster Ordnung, wobei

$$k = 5{\cdot}5 \times 10^{-3} \,.\, e^{\frac{-10{,}500}{RT}}.$$

Die niedrige Aktionskonstante wird mit Bezug auf die Potentialenergieoberflächen für die Reaktion

$$Ag^+CH_3^- \rightarrow Ag + CH_3$$

besprochen. Die entsprechende Reaktion zwischen Kupriverbindungen und den Bleialkylen verläuft anders und es wird ein wahrscheinlicher Mechanismus vorgeschlagen. Die Kombination von Kupferionen mit Bleitetramethyl oder -äthyl ist ein sehr wirksamer Polymerisationskatalysator und die Ketteneinleitung ist nicht die Folge der Bildung von freien Radikalen.

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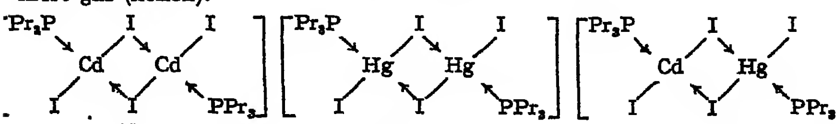
A PROBABLE EXAMPLE OF INORGANIC FREE RADICALS.

By F. G. Mann.

Received 21*st July*, 1947.

The study of free radicals has hitherto been confined almost exclusively to organic radicals. It is probable, however, that a wide field of development is available in the study of inorganic free radicals, particularly those containing metallic atoms.

An example of such radicals occurred in the investigation of " bridged " metallic complexes by Mann and Purdie.[1] It was found that tri-n-propylphosphine combined with cadmium iodide to give di-iodo-bis-(tripropylphosphine)-μ-di-iodo-dicadmium (I), m.p. 124°, in which the 4-covalent cadmium complexes are tetrahedral, and in which each cadmium atom has acquired 6 electrons to attain the electronic structure of the next inert gas (xenon).



(I) (II) (III)

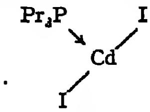
[1] *J. Chem. Soc.*, 1940, 1230.

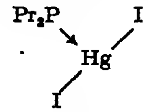
Mercuric iodide similarly gave di-iodo-bis(tripropyl-phosphine)-μ-di-iodo-dimercury (II), m.p. 114°, in which the metallic complexes are again tetrahedral, and in which the mercuric atoms have also acquired 6 electrons. Each of these products was a well-defined crystalline covalent compound, soluble in many organic solvents, and showing in such solvents a molecular weight corresponding closely to that required by the above formulæ.

When, however, warm alcoholic equimolecular solutions of the compounds (I) and (II) were mixed, the cadmium-mercury compound di-iodo-bis(tripropyl-phosphine)-μ-di-iodo-cadmium-mercury (III), m.p. 141°, crystallised out.

The formation of this compound is probably due to the compound (I) in alcoholic solution being in equilibrium with a very low concentration of the free radical (IA), and to the compound (II) being similarly in equilibrium with the free radical (IIA). These free radicals must be present only in small amount, as their presence cannot be detected by the normal cryoscopic molecular-weight determinations.

When solutions of the compounds (I) and (II) are mixed, however, these free radicals combine in unlike pairs to give the compound (III), because the latter is less soluble and presumably more stable (cf. the


(IA)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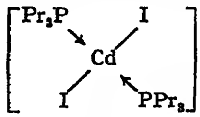
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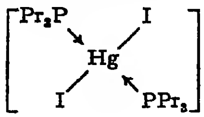
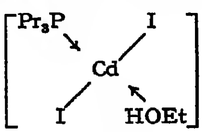
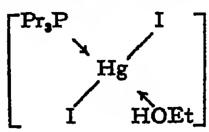

(V)

melting-points) than the compounds (I) and (II).

If a free radical is defined as a neutral group of combined atoms one of which possesses a deficiency of electrons, so that the groups can combine in pairs, then clearly (IA) and (IIA) are free radicals, as the normal saturated electronic condition of cadmium and mercury is that in which these atoms have acquired an additional 6 electrons, as in the compounds (I) and (II), and of course in the more simple unbridged compounds (IV) and (V). If, however, a free radical is defined more strictly as a neutral group of combined atoms one of which possesses an odd electron, then substances of type (IA) and (IIA) are not free radicals, but are members of a group of compounds intermediate in type between normal saturated molecules on the one hand and true free radicals on the other.

It must be emphasised, however, that very little indeed is known about the nature of the fission of compounds such as (I) and (II) in solution. It may be that the small degree of decomposition is due not to simple fission, but to the action of the alcohol, which may give compounds such as (IB) and (IIB) in very low concentration, the metal atoms thus retaining their 6 electrons, and that these unstable products (IB) and (IIB)


(IB)


(IIB)

then unite with loss of alcohol to give (III). If this is so, then no question of free radical formation arises.

The conditions that determine the formation of compounds such as (III) warrant further investigation therefore.

Résumé.

On souligne ici les vastes possibilités de développement qu'offre l'étude des radicaux libres minéraux, particulièrement ceux contenant des atomes métalliques,

tels les complexes métalliques " à pont", préparés précédemment par l'auteur et où il y a un groupe neutre d'atomes combinés, dont l'un est déficient en électrons.

Zusammenfassung.

Es wird ausgefuhrt, dass anorganische freie Radikale wahrscheinlich ein grosses entwicklungsfahiges Versuchsgebiet darstellen ; insbesondere Radikale, die Metallatome enthalten wie die früher vom Verfasser dargestellten Brücken-metallkomplexe, die eine neutrale Gruppe von gebundenen Atomen enthalten, von denen eines einen Elektronendefekt besitzt.

GENERAL DISCUSSION

Dr. M. J. S. Dewar (*Maidenhead*) said : Does not the failure of silver methyl to initiate polymerisation suggest rather that the methyl radicals are removed rapidly by the reaction, $Me\cdot + AgMe \rightarrow Ag + C_2H_6$, the silver methyl behaving as a kind of inhibitor ? A similar explanation would account for the formation of ethane in Stage 1 of the Cu^{++} reaction, $CuMe_2$ or $CuMe^+$ reacting with methyl radicals. In the second phase the liberation of free methane could be explained by the very low solubility of CuMe ; the methyl radicals formed by its decomposition can now attack the solvent to give CH_4 and an aldehyde, since the concentration of CuMe in solution is insufficient to remove them, and if a suitable monomer is present they can initiate polymerisation. It is extremely difficult to believe that free methyl radicals would not initiate polymerisation in styrene or methyl methacrylate, monomers which are known from copolymerisation experiments to react readily with radicals.

Dr. G. Salomon (*Delft*) said : On which experimental evidence is the assumption of an ionic carbon-metal bond based ? How are the differences in solubility for various metal alkyls explained ? Comparing structural formulæ and reactivity it seems sometimes more appropriate to consider a " degeneration of bond type " than the formation of true free radicals in solution.

Dr. C. H. Bamford (*Maidenhead*) said : I should like to illustrate a method by which the lower limits of certain velocity constants not readily accessible to direct measurement may be estimated. The principle of the method is to compare the rate of the rapid reaction (e.g. the combination of two methyls) with that of a competing reaction, and then to use data on vinyl polymerisation to obtain a lower limit for the latter reaction. Thus if we accept Bawn and Whitby's reaction scheme we can estimate a lower limit for the velocity constant (k) of (1) :

$$2CH_3 \rightarrow C_2H_6. \qquad (1)$$

Their (extrapolated) value at 0° C. for the velocity constant of the decomposition of AgMe in EtOH is $2 \cdot 5 \times 10^{-3}$ sec.$^{-1}$. Thus in a run in which $[AgMe] = 2 \cdot 7 \times 10^{-3}$ mol./l.$^{-1}$ the stationary concentration of methyl is given sufficiently accurately by :

$$k[Me]^2 = 2 \cdot 5 \times 10^{-3} \times 2 \cdot 7 \times 10^{-3} = 6 \cdot 8 \times 10^{-6}$$

or
$$[Me] = 2 \cdot 6 \times 10^{-3}/\sqrt{k}. \qquad (2)$$

Now
$$\frac{d(CH_4)}{dt} = k'[C_2H_5OH][Me] = 17 \cdot 4k'[Me] \qquad (3)$$

and
$$\frac{d(C_2H_6)}{dt} = 6 \cdot 8 \times 10^{-6} \qquad (4)$$

where k' is the constant for the reaction between methyl and alcohol-producing methane. Bawn and Whitby found no methane. Assuming they could detect 0·1 %, then we have from (3) and (4)

$$17 \cdot 4\, k'[Me] < 10^{-3} \times 6 \cdot 8 \times 10^{-6}$$

$$\text{or} \qquad \sqrt{k} > \frac{17\cdot4 \times 2\cdot6 \times 10^{-3}\, k'}{10^{-3} \times 6\cdot8 \times 10^{-6}} \qquad \text{by (2)}$$

$$\text{i.e.} \qquad > 6\cdot6 \times 10^{6}\, k'. \qquad (5)$$

Now the reaction between Me and EtOH is essentially similar to a chain-transfer process in vinyl polymerisation. Recent experiments by Mr. G. D. Lewis have shown that at 0° c. the absolute value of the transfer constant in vinyl acetate is 0·12 l. mol.$^{-1}$ sec.$^{-1}$. The methyl radical must be at least as active as the vinyl acetate radical, and since this factor seems of great importance in determining rates of transfer reactions (see remarks on Nozaki's paper), we may confidently put $k' > 0\cdot12$. Thus from (5) we obtain $k > 6\cdot3 \times 10^{-11}$ l. mol.$^{-1}$ sec.$^{-1}$. It would obviously be preferable to carry out the decomposition of AgMe in a solvent of which the transfer constant with vinyl acetate has been measured directly. If the reaction producing ethane is not the simple dimerisation as supposed by Bawn and Whitby, but some other reaction involving methyl, the lower limit for the velocity constant of the latter reaction could be found in the above way.

These results seem to show that the dimerisation involves little, if any, activation energy. Further, since the recombination in the gas phase probably has a low steric factor (see paper by Steacie, Darwent and Trost) the reaction under these conditions must involve three-body collisions. The value of k estimated above for the liquid phase corresponds to a minimum steric factor of about 10^{-2}. This would imply a minimum value of about 3×10^{-6} in the gas phase at *ca.* 200 mm. pressure, in good agreement with Steacie, Darwent and Trost's figure of 10^{-5}.

Dr. W. A. Waters (*Oxford*) said: Dr. Bawn's postulation of the unimolecular decomposition of dilute solutions of $AgCH_3$ to "free" methyl radicals, which are incapable of attacking the alcohol used as the solvent, seems to be rather abnormal. One would have expected that even at his low temperatures the free methyl radicals would have dehydrogenated surrounding molecules. The decomposition of $CuCH_3$ etc., is much more what one would have anticipated. These decompositions of organo-silver compounds deserve further study since Gilman and his colleagues have reported that AgC_6H_5 decomposed in solution to give over 70 % of diphenyl, whereas CuC_6H_5 under similar circumstances gave benzene. All previous studies of "free" phenyl radicals in solution have shown that it dehydrogenates the solvent and does not dimerise. Evidently there is much more to be learned about the decomposition of organo-metallic compounds in solution.

Dr. E. Warhurst (*Manchester*) said: With regard to Dr. Salomon's questions and in amplification of Dr. Bawn's remarks, I might mention that Mr. J. B. Taylor and myself at Manchester have been studying the physical properties of lithium alkyls. Preliminary work shows that liquid lithium *n*-butyl exhibits a very low vapour pressure ($\sim 2 \times 10^{-3}$ mm. at 70° c. and $\sim 4\cdot5 \times 10^{-4}$ mm. at 60° c.) and a very high latent heat of evaporation ($\sim$ 33 kcal./mole). From cryoscopic measurements in benzene solution, lithium ethyl is known to be associated to the extent of 6 or 7 molecules per cluster. Our experiments on lithium butyl accord with the view that this compound is also strongly associated in the liquid state and in solutions of hydrocarbons, due to a powerful dipole-dipole attraction between the strongly polar Li—C "heads" of the molecules. The complete miscibility of lithium butyl with hydrocarbon solvents (despite the large ionic character, $\sim$ 80 %, of the Li—C bond), can be explained on the basis of association. The heat of solution will be extremely small since the cluster-cluster cohesion in the liquid state is merely due to cohesion between hydrocarbon "tails", and the cluster-solvent cohesion is likewise an interaction between the hydrocarbon tails of a cluster and the solvent molecules.

There are a number of points which indicate that the Ag—C and Cu—C bonds are not as closely similar to Li—C bonds as Dr. Bawn suggests, the difference probably lying in the direction of a much-reduced ionic character for the Ag—C and Cu—C bonds compared with the Li—C bond. The ionisation potential and ionic size of lithium are considerably smaller than those of silver and copper, which tends to make the ionic state Li^+C^- more stable relative to the covalent state than obtains in the cases of Ag—C and Cu—C bonds. Further, the general reactivity of Li—C bonds appears to be much greater than that of Ag—C and Cu—C bonds. For example, lithium alkyls react vigorously with alcohols, whereas stable suspensions and solutions of Ag—CH_3 and Cu—CH_3 in alcohol can be obtained, as Bawn has shown

Dr. M. Szwarc (*Manchester*) (*communicated*): In a very interesting paper, Dr. Bawn and Mr. Whitby described the behaviour of Ag . CH_3. The striking facts are: the decomposition of Ag . CH_3 leads only to formation of C_2H_6 in proportion of $\frac{1}{2}$ mole C_2H_6 for one mole. $AgNO_3$ used; the reactions characteristic for CH_3 radicals have not been observed (i.e. formation of CH_4 by extraction of H atom from alcohol used as a solvent, and initiation of polymerisation); the decomposition gives first-order kinetics with an extremely small frequency factor.

It seems to me, that the lack of the characteristic reactions of the CH_3 radical leaves some doubts as to whether this radical is indeed formed (even at the extremely low temperatures applied by the authors). I would like, therefore, to suggest an alternative explanation of the above facts, which does not involve the formation of the CH_3 radical.

I assume that the bulk of the Ag . CH_3 formed in the reaction is in the form of a dimer $(Ag . CH_3)_2$. This assumption seems to gain some support from the fact that the Ag . Ph compound isolated by Kraus and Schmitz (*Ber.*, 1919, **52**, 2164) has a composition $(Ag . Ph)_2 . AgNO_3$. The decomposition of $(Ag . CH_3)_2$ is a unimolecular reaction, the transition state being formed by twisting, which brings the methyl groups near to each other. The extremely small frequency factor reflects the very low probability of attaining the above-mentioned transition state. The product of the reaction is, of course, C_2H_6 and in the proportion found in experiments. No CH_3 radical is formed and, therefore, we shall not expect any of the reactions characteristic for this radical.

Dr. C. E. H. Bawn (*Bristol*) said: In reply to Dr. Dewar, the absence of polymerisation in styrene does not preclude the formation of free methyl radicals, since it cannot be assumed that radicals formed at low temperatures will initiate this reaction. It may well be that the radical-initiation reactions require an appreciable activation energy, or propagation is difficult, and that the dimerisation reaction is the easier process.

The absence of reaction of methyl radicals with the solvent is not surprising, since the analogous reactions of these radicals with alkyl halides, aldehydes and ketones have activation energies of 8-15 kcal.

Silver phenyl is much more stable than silver methyl and decomposes in solution at a measurable rate at 60-80° c. Our preliminary studies show that appreciable formation of diphenyl occurs at 60° c., but that simultaneous dehydrogenation of the solvent, as stated by Dr. Waters, also occurs.

With reference to Dr. Warhurst's remarks, the silver and copper alkyls are insoluble in hydrocarbon solvents. The latter, like the lithium alkyl, reacts vigorously with alcoholic solvents at room temperature, but below − 30° c. the reaction is extremely slow.

In reply to Dr. Szwarc's suggestion of the formation of a dimer $(AgCH_3)_2$, I feel that the existence of molecules of this type is very improbable. Divalent silver is known in AgF_2 and in complex salts. The formation of CH_3—Ag—Ag—CH_3, which would require the promotion of one of the inner silver electrons to the O shell would have a linear con-

figuration, since *s-p* hybrids are concerned in bond formation. The configuration of the transition state would also be linear, and the production of ethane in one stage would therefore be unlikely. Owing to the instability of silver methyl, it is not possible to reach a definite decision as to the possibility of dimer formation, or association, by molecular weight determination. The measurements are, however, being carried out on the more stable silver phenyl.

Dr. C. E. H. Bawn and Mr. F. J. Whitby (*Bristol*) (*communicated*) : Recent investigation has shown that $CuCH_3$ reacts with methyl alcohol with the formation of methane, according to

$$CuCH_3 + CH_3OH \rightarrow CH_4 + Cu^+ + OCH_3^- . \qquad (1)$$

The cuprous ions formed react slowly with any excess lead tetramethyl present,

$$Cu^+ + Pb(CH_3)_4 \rightarrow CuCH_3 + Pb(CH_3)_3^+ \qquad (2)$$

and the reaction chain continues until all the lead alkyl is used up. The Cu^+ is partly destroyed with the formation of copper by the reaction

$$Cu^+ + Cu^+ \rightarrow Cu^{++} + Cu.$$

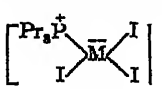
No aldehydes are formed in the absence of oxygen and reaction (1) is preferred to reaction (12) referred to in our paper.

Dr. J. H. van Santen (*Eindhoven*) said : We may consider the bond between a positive ion and a molecule like water from two extreme points of view. According to the covalent picture, an electron pair of the oxygen is donated to the positive ion whereas, from the heteropolar point of view, we have an interaction between a positive charge on the one side and a polar, polarisable molecule like water on the other side. I think that in the case of water the heteropolar model is quite satisfactory ; even the extreme case, that the positive ion is a hydrogen ion from another water molecule, can be fitted into this scheme (" hydrogen bond ").

If, however, water is replaced by the more polarisable molecule ammonia the heteropolar properties become less pronounced. In the case of the $[Co(NH_3)_6]^{3+}$ ion we may conclude from the magnetic behaviour that a considerable rearrangement of the electrons, has taken place.

In the case of a bond between a phosphine and a positive ion we can expect a still more covalent character than in the case of ammonia because of its higher polarisability, *a fortiori* for cadmium iodide, since here the heteropolar character will be rather weak. Yet I think that the transition from the hydrates on the one hand to Dr. Mann's compounds is so continuous that one should not call the latter radicals.

Mr. H. C. Longuet-Higgins (*Oxford*) said : I should like to make two small points in connection with Dr. Mann's paper. The first is to question whether the entities (IA) and (IIA) are necessarily intermediates in the reaction between (I) and (II) to give (III). Until more definite evidence is available it remains a possibility that the reaction proceeds through



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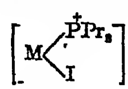


(VII)

ionic intermediates of the types (VI) and (VII). Both (I) and (II) might dissociate into ions of the type (VI) and (VII), and " cross-linking " between these ions could then give (III).

Secondly, according to Dr. Mann's definition of a free radical, a molecule such as the monomer of aluminium chloride is a free radical. Perhaps therefore it would be less confusing to reserve the term " free radical " for reactive molecules containing unpaired electrons, and refer to $AlCl_3$, etc., as electron-deficient molecules.

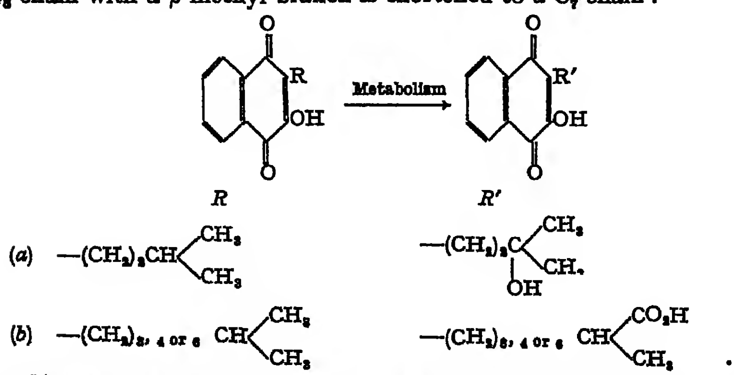
Dr. V. Gold (*London*) (*communicated*): Before any extension of definitions is adopted we should be certain that the current usage of terms is unsatisfactory. There is a distinction between free radicals and labile molecules, which is implicit in the names, and I would suggest that, as long as this is recognised, there is no need to modify the present definitions. A free radical is a polyatomic particle containing one or—less frequently—more unpaired electrons (in diradicals the two electrons concerned are not on the same atom in important valence bond structures); a labile molecule is an unstable molecular species possessing a short, transient life on account of its high reactivity. Thus, free radicals may be stable (e.g. Ph_3C, NO_2, NO) and labile molecules need not contain unpaired electrons (e.g. the carbonium cations formed during the unimolecular hydrolyses of alkyl halides). The molecules IA and IIA in Dr. Mann's paper represent the rather special case of labile lone-pair acceptor molecules which can undergo pairwise mutual co-ordination; they are *labile molecules* but *should not be called free radicals.* Dr. Mann's proposed definitions would lead to other difficulties. $(CO)^+$ and NO would not qualify as free radicals, the latter only because $(NO)_2$ does not exist although NO will react rapidly with other free radicals. On the other hand one can foresee that by a logical development of Dr. Mann's definition a reasonable case could be made out for regarding formic acid as a free radical as it will combine in pairs to form the dimer, a behaviour which is due to the fact that the acid hydrogen atom "possesses a deficiency of electrons" and therefore interacts with the carbonyl oxygen of the other molecule.

C.—OXIDATION-REDUCTION REACTIONS. CHROMIC ANHYDRIDE OXIDATION OF ALKYL SIDE-CHAINS.

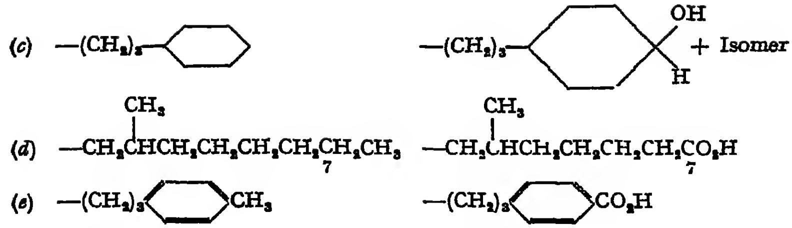
By Louis F. Fieser.

Received 12*th August*, 1947.

An investigation of the metabolism in man of a series of 2-hydroxy-3-alkyl-1 : 4-naphthoquinones of interest as potential curative antimalarial drugs disclosed the fact that most such substances undergo rapid oxidation in the liver to degraded products having an oxygenated side-chain but with the quinone nucleus still intact.[1] *Iso*alkyl side-chains suffer either hydroxylation to tertiary alcohols or end-methyl oxidation; a cyclohexyl group undergoes terminal hydroxylation to a secondary alcohol; a C_8-chain with a β-methyl branch is shortened to a C_7-chain:



[1] Fieser, Chang, Dauben, Heidelberger, Heymann and Seligman, *J. Amer. Chem. Soc.* (in press).



I have found that comparable side-chain degradation can be accomplished by oxidation of the acetyl derivatives with chromic anhydride.[2] Acidic products are extracted from an ethereal solution of the reaction mixture with soda and determined colorimetrically. The residual material is saponified and the more hydrophilic alcoholic or ketonic oxidation products separated from unchanged starting material by fractional extraction from ether with buffers of increasing alkalinity. Mixtures of acids are best processed by counter-current distribution of the esters between ether and a suitable buffer. Since the course of the oxidations can be followed by time-yield curves of acidic and non-acidic products, the effect of variations in the reaction conditions is easily established. By far the most efficient method found consists in agitating a glacial acetic acid solution of the substance to be oxidised with solid chromic anhydride at 20-25°; usually the starting material is completely consumed in about 45 min. and the total yield of oxidation products is 80-85 %. When the oxidation is conducted by the classical procedure in a homogeneous solution containing 10 % water the total yield is never over 57 % and some 5 % of starting material is still present after 24 hr.

Side-chain oxidations accomplished by the simple and efficient non-aqueous procedure are as follows (the structures were established by analysis, synthesis, or degradation):

(1) $—(CH_2)_nCH(CH_3)_2 \longrightarrow —(CH_2)_nC(OH)(CH_3)_2 + —(CH_2)_{n-1}CO_2H$

$n = 2, 4, 6, 7$; A: $n = 2, 4, 6$; B: $n = 2, 4, 6, 7$

(2) $—(CH_2)_8CH(CH_3)_2 \longrightarrow —\underbrace{(CH_2)_2(CH_2)_6}_{O—2H}CH(CH_3)_2 + —(CH_2)_7CO_2H$

M—2284

(3) $—C_{10}H_{21}—n$ (M—273) $\longrightarrow$ $\begin{cases} —CH_2CH_2CH_2CH_2CH_2CH_2\underset{7}{C}OCH_2CH_2CH_3 \\ —(CH_2)_nCO_2H \end{cases}$

$n = 2, 3, 4, 5, 6, 7$

(4) $—C_{17}H_{35}—n$ (M—2256) $\longrightarrow$ $—C_{17}H_{33}O$

(5) $—CH_2CH(CH_3)C_6H_{13}—n$ (M—285) $\longrightarrow$
(A) $—CH_2CH(CH_3)CH_2CH_2CH_2CH_2\underset{7}{C}OCH_3$
(B) $—CH_2CH(CH_3)CH_2CH_2CH_2CH_2\underset{7}{C}O_2H$
(C) $—CH_2CH(CH_3)CH_2CH_2CH_2\underset{6}{C}O_2H$
(D) $—CH_2CH(CH_3)CH_2\underset{4}{C}O_2H$

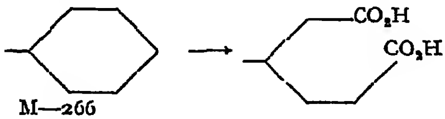
[2] Fieser, *J. Amer. Chem. Soc.* (in press).

(6) $—(CH_2)_8CO_2CH_3$ M—1917 $\longrightarrow \begin{cases} \text{(A)} & —(CH_2)_4CO_2H \\ \text{(B)} & —(CH_2)_3CO_2H \\ \text{(C)} & —(CH_2)_2CO_2H \end{cases}$

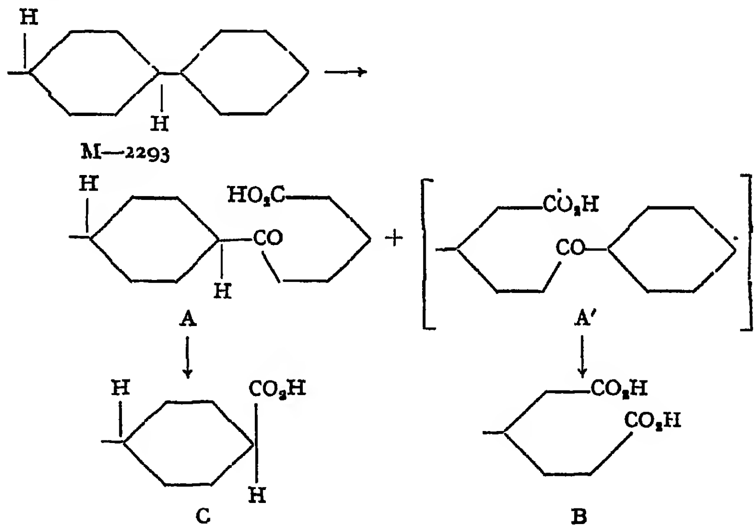
(7) $—CH_2CH_2CH_2CH_2CH_2C_6H_5 \longrightarrow —CH_2CH_2CH_2CH_2COC_6H_5$
M—2276

(8) $—CH_2CH_2CH_2C_6H_4CH_3—p \longrightarrow \begin{cases} \text{(A)} & —CH_2CH_2COC_6H_4CH_3—p \\ \text{(B)} & —CH_2CH_2CH_2C_6H_4CO_2H—p \end{cases}$
M—1952

(9) $—CH_2CH_2CH_2$—Cyclohexyl $\longrightarrow$ $—CH_2CH_2CO_2H$
M—1916

(10) 

M—266

(11) 

(12) $—CH_2C(CH_3)_3$: no side chain oxidation, 85 % recovery.
M—1934

Three of the oxidation products (1A, $n = 2$; 5B; 8B) are identical with products of metabolism in the human liver. A fundamental difference is that end-methyl groups are sometimes attacked in biological oxidations but are resistant to chromic anhydride oxidation except when activated (8B); the side-chain $—CH_2C(CH_3)_3$ is completely resistant to attack by chromic anhydride. A striking observation is that a normal C_{10}-chain (3) and a β-branched C_8-chain (5) are attacked preferentially at position 7 in the chain and converted into *eta*-keto derivatives. It may be a coincidence that two of the biological oxidations (*c* and *d*) may also be described as *eta*-oxidations. In the chemical oxidation, at least, the preferential point of attack seems to be at a certain distance from the quinone nucleus, regardless of the length of the chain. A possible explanation is that the oxidant and the quinone form a complex in which the metallic oxide or ion is bound to either the 4-keto or 2-acetoxy group and can attack only a portion of the coiled side-chain that can become oriented close to it in space.

Another reaction that appears novel is the production of tertiary alcohols from *iso*alkyl side-chains (1). That the alcohols of type A are the precursors of the acids B was inferred from time-yield curves and established by direct conversion, and hence oxidative fission of tertiary alcohols is another reaction realised by the anhydrous procedure. A further reaction is the smooth fission of alicyclic rings to keto acids (11). These reactions probably are not specific to the non-aqueous procedure, but the fact that they have remained obscure or unknown points to a greater efficiency of the present procedure over the classical one. In a current investigation of compounds other than quinones, the procedure has been found applicable to the oxidation of aromatic, hydroaromatic, and paraffinic hydrocarbons, to higher fatty acids, and to a variety of carbinols.

Westheimer and Novick [3] interpreted the kinetics of the chromic acid oxidation of *iso*propyl alcohol in dilute aqueous solution in terms of an ionic mechanism. In a qualitative study of oxidations effected by chromic anhydride in a very dilute solution in glacial acetic acid, Waters [4] found that some oxygen was absorbed in those instances where a reaction occurred and suggested that the reaction proceeds by an oxygen-propagated free-radical mechanism. When a typical naphthoquinone oxidation (M-266 acetate) was conducted in the Warburg apparatus, about 0·03 mole of oxygen per mole of naphthoquinone was consumed in 1 hr., about half of it in the first 15 min. A large-scale oxidation conducted in a nitrogen atmosphere gave the same product, and in substantially the same yield, as one conducted in a vigorously-stirred mixture exposed to air. Oxygen absorption in this instance thus appears to be a minor side reaction not essential to the main oxidation.

Résumé.

On discute l'oxydation chromique des chaînes latérales alcoyles ; la dégradation de la chaîne latérale est comparable à l'oxydation rapide de ces composés dans le foie, où ils ont une chaîne latérale oxygénée avec un noyau quinonique intact. On indique la méthode d'oxydation par un procédé efficace non-aqueux et la nature des produits formés.

Zusammenfassung.

Die Oxydation von Alkylseitenketten durch Chromtrioxyd wird erörtert; Abbau der Seitenkette gleicht der schnellen Oxydation dieser Verbindungen in der Leber darin, dass die Produkte eine oxydierte Seitenkette enthalten aber einen unangegriffenen Chinonkern. Es wird die Oxydationsmethode durch eine nichtwässerige Prozedur mit guter Ausbeute beschrieben und die Produkte werden angegeben.

Department of Chemistry,
Harvard University,
Massachusetts.

[3] Westheimer and Novick, *J. Chem. Physics*, 1943, 11, 506.
[4] Waters, *J. Chem. Soc.*, 1946, 1151.

ANIONIC INTERMEDIATES IN REDUCTION BY NASCENT HYDROGEN.

BY ARTHUR J. BIRCH.

Received 11*th August*, 1947.

The aim of this paper is to show that reduction by "nascent" hydrogen can be explained in all its aspects if it is assumed that the essential stage is the addition of two, or more rarely, one electron to give a charged transition complex. In some cases, e.g. benzophenone, there is no doubt that limited amounts of reducing agent give anion-radicals; reductions at the dropping mercury electrode may also take place in one-electron stages, but more often in two, for example with polycyclic hydrocarbons.[1, 2] An examination is made here of the reductions fairly certainly involving two electrons.

With organic compounds two types of reaction may be distinguished: addition of electrons to form a divalent anion in the case of an unsaturated system, or fission of the molecule with formation of two anions. Both may be formally considered on the same lines since they involve the disappearance of a bond and the production of two negatively charged atoms or groups. Whether the process takes place depends on whether there is sufficient energy available, and it is therefore necessary to arrive at some idea, even if only qualitatively, of the energy factors involved.

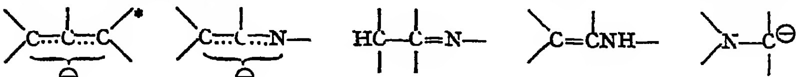
The driving energy must come from the electrons supplied by the reducing agent, measured by their potential, and it may be assisted by favourable energy changes due to alterations in bond energy or resonance. The energy used up may conveniently be divided into that required to produce the charged atoms, and other unfavourable bond or resonance changes, including the mutual influence of the charges.

The relative energies required to produce a single negative charge in different systems can be roughly determined by examining the acidities of the "acids" to which the anions give rise by addition of a proton: the greater the acidity the lower the energy. The ideas thus gained can then be extended to the relative energies of the similar anions formed during reduction. For saturated carbon atoms it appears from general principles, confirmed by the work of Morton and others,[3, 4] that the acidity of an attached proton should decrease with increased degree of alkylation, i.e. the energy of a negatively charged carbon atom will be higher the greater the number of alkyl groups attached to it. In a system in which the charge is de-localised (such as the allylic anion (I)) the acidity of the proton is greatly increased, and the charge energy lowered. In considering the effect of substitution on such a system it is necessary to take account of both ends of the ion, since the charge resides to some extent on both the end carbon atoms. It appears that, to a first degree of approximation, the energy of formation of (I) is increased by increasing the degree of alkylation and decreased by increasing the degree of arylation

[1] Wawzonek and Laitinen, *J. Amer. Chem. Soc.*, 1942, **64**, 1767, 2365.
[2] Wawzonek and Fan, *ibid.*, 1946, **68**, 2541.
[3] Morton, *Chem. Rev.*, 1944, **35**, 8.
[4] Fenton and Ingold, *J. Chem. Soc.*, 1929, 2338.

of the end carbon atoms.[5, 6] The direct metallation results of Morton and others [7, 8] would appear to confirm this idea.

The effect of hetero-atoms on acidity is clear from the known order CH < NH < OH, giving the order of energies $C^- > N^- > O^-$. Thus, if the hetero-atom is present in an allylic anion (II) the acidity of an attached H will be greatly increased over that in the carbon system, no matter whether the acid considered is (III) or (IV). Owing to the unshared electrons on the hetero-atom there is the possibility that the energy of a negative charge on an adjacent carbon atom as in (V) may be raised; the inductive effect of groups like methoxyl tends, however, to raise acidity, and both effects appear to come into play according to circumstances.



(I) (II) (III) (IV) (V)

If two negative charges are present, as in many reduction intermediates, the energy of the anion will be further raised by a factor due to their interaction.

With these ideas in mind let us consider the effect first on the primary reduction process—electron addition—and then on the secondary processes—proton addition or dimerisation—of altering the reducing agent, the solvent, and the nature of the substance reduced.

Reducing Agent.—Leaving out of consideration factors such as convenience of application, the most important characteristic of the electron source is its potential. This is sufficiently obvious and is well illustrated by metal and polarographic reductions.[10]

Influence of Solvent on Primary Reduction.—The nature of the solvent is often critical not only for the subsequent reactions of the transition complex, but for its formation as well. For example, sodium and alcohol in petrol are incapable of reducing anisole, but in liquid ammonia or ethylenediamine a good yield of 2 : 5-dihydroanisole is obtained.[9, 11, 12] The favourable influence of solvents like alcohols or amines is probably due to their anionoid character. This is manifested particularly in the case of ammonia, which is a very useful solvent for promoting the formation of alkali-metal salts of even such weak acids as unsaturated hydrocarbons [8, 9] as well as for reductions, and the two aptitudes are obviously linked. The ability of ammonia and some amines to dissolve alkali metals unchanged is also favourable and avoids any necessity for considering surface reactions in such cases.

The acidity of the solution is also of the greatest importance, since it determines the energy required to detach protons from it. Alkylbenzenes and anisoles are not reduced by sodium in liquid ammonia except in the presence of alcohol.[13, 14] The divalent anion, e.g. (VI) evidently requires such a high energy because of the high resonance energy of the benzene ring that it cannot be produced as such, that is, as part of the sodium salt formed of (VI) and two sodium cations. However, in the presence of alcohol the ion can be formed as part of a transition state to the energy of which the exothermic addition of protons from the alcohol contributes. Ammonia cannot

(VI)

[5] Birch, *J. Chem. Soc.*, 1945, 809. [6] Birch, *ibid.* (in press).

[7] Morton, *J. Amer. Chem. Soc.*, 1945, **67**, 2224.

[8] Levy and Cope, *ibid.*, 1944, **66**, 1684; Campbell and Young, *ibid.*, 1947, **69**, 688.

* To avoid confusion the atoms being considered are the only ones shown; the bonds are to be taken as joined to hydrogen or alkyl groups.

[9] Birch (unpublished work).

[10] Kolthoff and Lingane, *Polarography* (Interscience, N.Y., 1941).

[11] Birch, *Nature*, 1946, **158**, 585. [12] Birch, *J. Chem. Soc.*, 1946, 593.

[13] Birch, *ibid.*, 1944, 430. [14] Birch, *ibid.*, 1947, 102.

replace alcohol because of the much higher energy required to detach protons from it. Neither can the alcohol be replaced by the very acidic ammonium chloride, since here the competing reaction which evolves hydrogen gas is favoured. The acidity of the solution, particularly in water, may also affect the primary reduction by altering the nature of the substance reduced: indole for example is reduced only in strongly acid solution, and it is probably the salt which reacts.[15]

Reduction in the presence of a proton source is greatly affected by solubility, since if the substance is too insoluble metal reductions give merely hydrogen gas. This is clearly why many substances fail to reduce in liquid ammonia,[13] which may often be replaced by ethylenediamine.[9] The presence of impurities is often critical also. Metallic iron in sodium amalgam [16] or liquid ammonia [13] is harmful, probably because it catalyses the reaction which leads to hydrogen gas.

Temperature.—The yield in a reduction often increases with rise in temperature, presumably because of the greater energy available in the system. This can be seen by comparing the yields of dihydroanisole obtained with the same amounts of reducing agent in various petrol fractions: b.p. 40-60°, 0·3 %; b.p. 60-80°, 4·3 %; b.p. 100-120°, 7·5 %.

Reducibility and Structure.—UNSATURATED SYSTEMS.—It is possible to reduce $>C{=}O$, $>C{=}N{-}$, $-N{=}N-$, $-C{\equiv}C-$, and $-C{\equiv}N$ but not $>C{=}C<$. The energy of formation of $>\overset{\ominus}{C}-\overset{\ominus}{C}<$ would obviously be high, and replacement of one of the charged carbon atoms by $N^{\ominus}$ or $O^{\ominus}$ would give a more-easily-reached energy value. The reduction of $-C{\equiv}C-$ must be ascribed to the high energy content of this group compared with $>C{=}C<$; and it may also be noted from the metallation results of Morton [7] that the acidity of $>C{=}\dot{C}H$, although less than that of $>C{=}\overset{|}{C}CH$ is higher than that of $-\overset{|}{\underset{|}{C}}H$, i.e. the energy of $>C{=}\overset{\ominus}{C}-$ will be less than that of $-\overset{|}{\underset{|}{C}}{\ominus}$. The formation of the pure *trans*-ethylenes is further evidence for the intervention of a charged intermediate.[18]

Systems containing conjugated carbon-carbon double bonds are reducible with reagents of sufficiently high potential because of the delocalisation of the charges, although high resonance energy, as in the benzene ring, may make reduction difficult. Fused benzene rings are more easily reducible, not only because the resonance energy for a given ring is lower, but because the charge can be distributed over the whole molecule. The effect of substitution on the reduction potential of a double bond can be seen from the following results: [1] $PhCH{=}CH_2$, − 2·343 v.; $PhCH{=}CHCH_3$, − 2·537 v.; $PhCH{=}CHPh$, − 2·140 v.; $Ph_2C{=}CH_2$, − 2·258 v.; $PhCH{=}CHCH{=}CHPh$, − 1·981 v.; $Ph_2C{=}CHPh$, − 2·118 v.; $Ph_2C{=}CPh_2$, − 2·046 v. Two phenyl groups on one end of the double bond have less effect than one on each end, since in the former case they can stabilise only one charge. Ease of reduction is increased if there is present a hetero-atom such as N or O upon which the charge can reside (e.g. quinoline or benzoic acid) in the same way that acidity is raised if these atoms are present in an allylic ion. . However, if the hetero-atom is present in a five-membered ring such as in indole [9] or 2-methylfuran [5] where its unshared electrons are involved in the aromatic resonance,

[15] v. Braun and Sobecki, *Ber.*, 1911, 44, 2159.
[16] Willstaetter, Seitz and Bumm, *ibid.*, 1928, 61, 871.
[17] Young and Eisner, *J. Amer. Chem. Soc.*, 1941, 63, 2113.
[18] Henne and Greenlee, *ibid.*, 1943, 65, 2021.

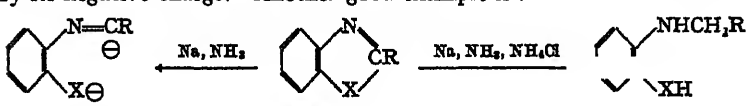
reduction is inhibited. This is due to the more-loosely-held character of the π-electrons, compared with a benzene ring, and also to the fact that the charge cannot reside on the hetero-atom itself (compare the low acidity of HC—N< with the high acidity of HC—C=N—).

Groups which tend to charge the conjugated system negatively such as alkyl groups, also lower the ease of reduction. This is clearly seen with the benzene ring. The following relative yields of dihydro-derivatives were obtained with potassium under the same conditions: anisole, 7·5 %; 3-methylanisole, 1·7 %; 3 : 5-dimethylanisole 0·14 %.[9] The same effect can be noted on the potentials of benzaldehydes substituted by the following groups in the *para*-position: Cl, − 1·14 v.; H, − 1·20 v.; CH_3, − 1·25 v.; OCH_3, − 1·30 v.[19]

The methoxyl group in a benzene ring can exercise either an activating or de-activating influence according to its position: 1-methoxynaphthalene reduces in the unoccupied ring, 2-methoxynaphthalene in the occupied ring (compare elimination reactions below and also [9, 14]).

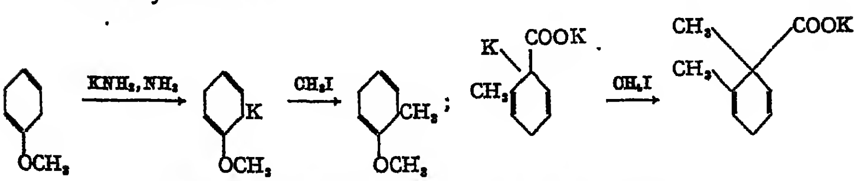
Elimination Reactions.—The hydrogenolysis of allyl alcohols by sodium and alcohol in ammonia seems to involve mesomeric anions.[5] As expected, increased alkylation or decreased arylation of both ends of the system decreases the ease of reduction. The effect of substituents in the benzene ring is best studied by the hydrogenolysis of benzyl alcohols [5, 9] or the fission of ethers,[14, 20] and in both cases the expected de-activating effect of alkyl groups and the activating effect of carboxyl or carbonyl groups is encountered. With methoxyl groups the position is more complicated. With a methoxyl in the *ortho*-position to the negatively charged atom there is an activating influence, in the *para*-position there is a strong de-activating influence. It may also be noted that 2 : 5-dihydroanisoles metallate in the 2-position,[6] and anisoles invariably *ortho* to the methoxyl.

Effects of the Solvent on the further Course of Reduction.—If the solvent is a weak enough acid—ammonia for example—the metal addition compound may be stable. This is so with naphthalene and sodium in ammonia at − 70°, and the product is protected from further reduction by its negative charge. Another good example is: [21]



(X = O, S)

If the hydrogenated product is formed in the presence of either strong acid or alkali it may be further reduced in consequence of bond isomerisation. With the $\alpha\delta$-dihydrobenzenes, for example, the conjugated $\alpha\beta$-dihydrobenzenes are formed in liquid ammonia in the presence of metal amide, and these are then reduced to tetrahydrobenzenes if excess reducing agent is present. Metal salts are undoubtedly formed as intermediates in this isomerisation, as can be proved by acting on the ammonia solution with methyl iodide: [9]



[19] Baker, Davies and Hemming, *J. Chem. Soc.*, 1940, 692.
[20] Sartoretto and Sowa, *J. Amer. Chem. Soc.*, 1937, 59, 603.
[21] Knowles and Watt, *J. Org. Chem.*, 1942, 7, 60.

Using the principles already outlined to determine the most acidic hydrogen atom, it is possible to predict the nature of the conjugated compounds.[6]

The degree of availability of protons in the solution may also decide whether the product is hydrogenated or dimerised. For example 1 : 1-diphenylethylene with sodium in ammonia gives 1 : 1 : 4 : 4-tetraphenylbutane, but in presence of the more acidic ethylaniline 1 : 1-diphenylethane is formed.[22] Similarly pyridine with sodium in ammonia gives chiefly a dihydrodipyridyl, but with addition of alcohol a dihydropyridine.[9]

Position of Addition of Protons to a Mesomeric Anion.—In a mesomeric ion there are at least two positions to which a proton can add. When such additions are *reversible* the product is the thermodynamically stable isomer,[23] but this is not necessarily or even usually true for *non-reversible* additions. For reductions with alkali metals in liquid ammonia the general rule seems to be that protons add to the form of the ion which contributes most to the resonance, i.e. has the lower energy as arrived at on the basis of charge stability. For example, in reduction of the benzene ring the charges add protons in the $\alpha\delta$-positions and tend to avoid alkyl and methoxyl groups and to seek carboxyl groups; while in polycyclic compounds they react in positions where they are most stabilised by resonance.[13] With mesomeric allylic ions the form which has the charge on the least alkylated or most arylated carbon atom reacts.[5] In other reductions, for example, of diene acids in aqueous solution,[24] a mixture of products is obtained, although even in these cases by increasing the degree of alkylation of a position the amount of proton addition there is lowered. Also by increasing the charge on the carboxyl by salt formation a proton is added to a greater extent in the more remote position :[24]

Solvent	% of 1 : 2-dihydro-isomeride formed from	
	$CH_2{=}CHCH{=}CHCOOH$	$CH_3CH{=}CHCH{=}CHCOOH$
Water + $NaHCO_3$	0	40
Water + CH_3COOH	18	55

The factors which influence the irreversible addition of an addendum to one or other end of an allylic ion are not known, but the subject is of the greatest importance, involving among other things the ratio *ortho/para* in substitution. In a discussion of this character, a little speculation may perhaps not be out of place.

The critical energy required to produce a transition state containing a negative ion may conveniently be divided into two parts: that associated with the formation of the ion and that associated with addition of the addendum. If the ion is not symmetrical one of its forms must have a lower energy than the other and approximate more to the mesomeric ion. Neglecting as hitherto any purely steric factors, it seems probable that the addition of an addendum requiring little further critical energy should take place chiefly on the lower energy form of the ion, i.e. to the end where the charge is most stable. However, if this critical energy rises too high, or the total amount of energy for the process falls too low, it might be expected that the higher energy form of the ion, which presumably has its charge in a more reactive condition, should begin to add the addendum, although the overall reaction velocity should, of course, fall.

These ideas can be illustrated by reactions of butenyl halides, the reduction of which evidently goes through a mesomeric anion, since butenyl and methyl vinyl carbinyl halides give the same mixture of butene-1 and butene-2 (the energy difference between these halides must be small since they form about an 85/15 equilibrium mixture). The ratio of butene-1

[22] Ziegler, Colonius and Schafer, *Annalen*, 1929, 473, 36.
[23] Branch and Calvin, *The Theory of Organic Chemistry* (Prentice-Hall, N.Y., 1941), p. 281.
[24] Burton and Ingold, *J. Chem. Soc.*, 1929, 2022.

to butene-2 is found to decrease with increasing reduction potential of the *metal employed, i.e. with increasing* energy available.[25] *This fits* with the idea that the form $CH_3CH{=}CHCH_2\ominus$, having its charge on the lower alkylated carbon atom, and its double bond in the more highly alkylated position, should have a lower energy than $CH_3CH\ominus CH{=}CH_2$. Further, the reaction of mixtures of the isomeric chlorides and of the isomeric bromides with zinc give mixtures of butenes in which the proportions are constant for a given halogen derivative, but invariably contain more butene-1 with the chlorides. This agrees with the idea that a bromine anion is more readily detached than a chlorine anion, thus leaving more energy in the allylic ion itself. Moreover, if the Grignard reagents from the chlorides or bromides are decomposed with water, the mixtures of butenes obtained are identical: in this case the halogen is detached during the formation of the reagent and its nature does not affect the allylic ion.[17] Reactions of butenyl Grignard reagents with reagents like ketones or allyl halides, for which the critical energies must be higher than for the addition of a proton, invariably produce reaction with the charge in the secondary, not the primary position. The observations of Ziegler [26] on the addition of lithium alkyls to butadiene also bear on the problem. Here there is initial formation of a mesomeric ion $RCH_2\underbrace{CH\mathrel{\overline{\cdots}}CH\mathrel{\overline{\cdots}}}_{\ominus}CH_2$ and this adds to the end of more butadiene molecules, the product in each case terminating in a mesomeric ion of the same form as the initial product. These react with water giving compounds terminated by $-CH{=}CHCH_3$, i.e. the proton adds to the more stable charge position. However, the position of addition of another butadiene molecule depends on the temperature. At about $+100°$ the addition is 1 : 4-, i.e. to the lower energy form, while at $-80°$ it is chiefly 1 : 2-, i.e. to the higher energy form. This must be related to the fact that at the higher temperature there is more energy available and thus more addition to the more stable form of the ion.

Résumé.

On peut expliquer la réduction par l'hydrogène naissant, en supposant que l'étape essentielle est l'addition de deux—ou plus rarement d'un—électrons pour donner un complexe de transition chargé. On examine certaines réductions qui, pense-t-on, comportent deux électrons et l'on discute l'influence du solvant sur la première étape et sur les étapes suivantes de la réduction, la réductibilité plus ou moins grande en fonction de la structure, et la position d'addition des protons à un anion mésomère.

Zusammenfassung.

Reduktion durch naszierenden Wasserstoff wird durch die Annahme erklärt, dass die ausschlaggebende Stufe die Addition von zwei Elektronen oder seltener von einem Elektron ist, wodurch ein elektrisch geladener Übergangskomplex entsteht. Reduktionen, von denen anzunehmen ist, dass zwei Elektronen beteiligt sind, werden untersucht; der Einfluss des Lösungsmittels auf den primären und den weiteren Verlauf der Reduktion, die Beziehung zwischen der Reduzierbarkeit und der Struktur, sowie die Stellung in einem mesomerin Anion, an der Addition eines Protons eintritt, werden besprochen.

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[25] Young, Kaufman, Loshokoff and Pressman, *J. Amer. Chem. Soc.*, 1938, **60**, 900.
[26] Ziegler, *Annalen*, 1938, **542**, 90.

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS.

V. THE INHIBITORY EFFECT OF PHENOLIC COMPOUNDS ON THE THERMAL OXIDATION OF ETHYL LINOLEATE.

By J. L. Bolland and P. ten Have.*

Received 13th January, 1947.

In a previous paper in this series [1] a kinetic analysis of the oxidation of ethyl linoleate in presence of a representative phenolic inhibitor, hydroquinone, was carried out in some detail. The two main conclusions drawn were (*a*) that the hydroquinone intervened in the oxidation chains by interacting with one chain carrier, RO_2—, and (*b*) that the hydroquinone was removed from the oxidising olefin in such a way as to correspond quantitatively to its chemical conversion (presumably to quinone) as a result of the termination reaction. In this paper, the choice of inhibitor is extended to other phenolic compounds, selected in such a way as to enable the chemical nature of the interaction with RO_2— to be identified by kinetic methods, and at the same time to bring to light additional ways in which diverse members of this group may interfere in the oxidation of olefins.

Some comparisons of the effectiveness of various phenols as inhibitors in different oxidation systems are available.[2-6] These investigations almost invariably employ the length of induction period, which precedes the oxidation of peroxide-free hydrocarbon, as criterion for antioxidant efficiency: while this is obviously the type of measurement which is of most direct interest from the practical point of view, the oxidation mechanism under these conditions is undoubtedly complicated by the variety of ways in which oxidation may be initiated, and by the fact that in the course of the induction period the rate of chain initiation is by no means constant. Kinetically a far more satisfactory system is obtained by introducing peroxides into the hydrocarbon to be oxidised (either by preliminary autoxidation or by deliberate addition of pure simple peroxides): the oxidation chains are then initiated in one known way only and at a rate which is increased relatively little by the subsequent oxidation. In comparing a series of phenols, we have therefore concentrated attention on measuring the diminution in oxidation rate resulting from their addition to rapidly-oxidising ethyl linoleate and methyl oleate.

Experimental.

Materials: 1:4-Naphthohydroquinone was prepared by reduction of 1:4-naphthoquinone with $SnCl_2$,[7] followed by recrystallisation from

* Seconded by the Netherlands Indies Govt. to the B.R.P.R.A.

[1] Bolland and ten Have, *Trans Faraday Soc.*, 1947, 43, 201.

[2] Egloff, Lowry, Morrell and Dryer, *Ind. Eng. Chem.*, 1933, 25, 804.

[3] Jeu and Alyea, *J. Amer. Chem. Soc.*, 1933, 55, 575.

[4] Olcott, *ibid.*, 1934, 56, 2492.

[5] Bickoff, Williams and Sparks, *Oil and Soap*, 1944, 22, 128.

[6] Süllmann, *Helv. Chim. Acta*, 1943, 26, 1114.

[7] Russig, *J. prakt. Chem.*, 1900, 62, 32.

benzene. The remaining phenols were commercial products,† carefully purified by repeated crystallisations. The methyl oleate was prepared (by Dr. D. A. Sutton) from olive oil; before use it was purified by molecular distillation [8] (at 65° c.) and chromatographed on an alumina column.

Oxidation rates were normally measured by the technique described in Part IV. In a few experiments where the measurement of very small initial rates of oxidation was required, a simple constant-volume apparatus similar to the Warburg manometer was used. Octoil was used as manometric liquid.

The Relative Efficiency of Phenolic Antioxidants.—Initial rates of oxidation of ethyl linoleate containing dibenzoyl peroxide or linoleate hydroperoxide as oxidation initiator, and a phenol as inhibitor are collected in Table I. The kinetics of oxidation in presence of each of the phenols has not been studied in detail, though in each case the effect of antioxidant concentration has been sketched. The temperature used throughout was 45° c. and the oxygen pressure 30 mm.

TABLE I.

Antioxidant.	Peroxide.	[AH].	[Peroxide.]	R_U.	R_a.	K.
		(moles/mole ester)		(moles O_2/mole ester/min.)		
		$\times 10^4$	$\times 10^2$	$\times 10^4$.		
Resorcinol	Bz_2O_2	4·14	3·20	2·30	1·48	116
		19·5	2·61	2·09	0·225	108
*		302	2·69	2·13	0·020	—
β-Naphthol	,,	17·0	3·06	2·26	0·135	44·5
		81·4	2·50	2·04	0·023	43
*		195	2·95	2·22	0·010	—
p-Methoxyphenol	,,	1·86	3·18	2·29	0·550	19·4
		5·82	2·81	2·16	0·152	18·6
		16·0	2·86	2·18	0·060	20·2
		25·7	2·35	1·99	0·039	25
α-Naphthol	,,	2·36	2·85	2·18	0·118	5·8
		14·0	4·11	2·57	0·029	6·1
Catechol	,,	0·61	3·05	2·25	0·220	2·65
		2·02	2·67	2·11	0·064	2·84
Pyrogallol	,,	0·68	2·98	2·22	0·080	1·10
		1·98	2·85	2·18	0·029	1·24
Toluhydroquinone	,,	0·46	2·51	2·04	0·099	1·10
		0·88	2·56	2·06	0·058	1·20
Hydroquinone		See Table I, Part IV.				1·70
*	,,	305·0	3·02	2·23	0·010	—
	ROOH	See Table II, Part IV.				2·75
Tri-methyl		0·89	17·7	2·30	0·032	0·48
hydroquinone	,,	3·65	17·7	2·30	0·008	0·5
1 : 4-Naphthohydroquinone	,,	0·77	17·7	2·30	0·005	0·07

In Table I, R_U and R_a are respectively the initial rates of oxidation in absence and in presence of an inhibitor concentration of [AH]. The initial rates of oxidation in presence of hydroquinone were found experimentally [1] to conform to the relation

$$R_a = K \cdot \frac{R^2_U}{[RH][AH]} \qquad (1)$$

† We are indebted to Messrs. Roche Products Ltd., for the gift of a sample of trimethylhydroquinone.

[8] Farmer and Sutton, *J. Soc. Chem. Ind.*, 1946, 65, 164.

where [RH] represents the linoleate concentration, and K is a constant, which is practically independent of whether the oxidation is initiated by dibenzoyl peroxide or ethyl linoleate peroxide. The form of this kinetic equation is consistent with the following reaction scheme:

Initiation	$\left.\begin{matrix} ROOH \\ Bz_2O_2 \end{matrix}\right\} \rightarrow R\text{—} \text{ or } RO_2\text{—}$	R_i	
Propagation	$R\text{—} + O_2 \rightarrow RO_2\text{—}$	k_2,	(R2)
	$RO_2\text{—} + RH \rightarrow ROOH + R\text{—}$	k_3,	(R3)
Termination	$RO_2\text{—} + AH \rightarrow$ stable products	k_9,	(R9)
	$RO_2\text{—} + RO_2\text{—} \rightarrow$ stable products	k_6,	(R6)

the reaction (R6) being only of importance when the antioxidant is absent. This kinetic analysis leads to the relation

$$K = \frac{k_6}{k_3 k_9} \qquad (2)$$

Now k_9 is undoubtedly the most direct quantitative measure of the chain-breaking efficiency of an antioxidant. Since k_3 and k_6 depend only on the structure of the olefin, the relative efficiencies of a series of antioxidants, are given by the reciprocal of K—assuming that the mechanism by which the antioxidants act is in each case the same as for hydroquinone. While the assumption is not fully justified here, the data in Table I do indicate that the rate of oxidation is inversely proportional to [AH] in presence of at least 8 of the 9 phenols; in the case of 1:4-naphthohydroquinone, experimental difficulties outlined below precluded measurements over a range of [AH].

TABLE II

Antioxidant.	Relative Efficiency.	E_0 (v.).
(*a*) Phenols—		
Resorcinol	0·016	1·179
β-Naphthol	0·077	1·153
p-Methoxy-phenol	0·170	0·984
α-Naphthol	0·56	0·933
Pyrogallol	3·0	0·676
(*b*) Hydroquinones—		
Catechol	0·63	0·810
Hydroquinone	1·00	0·715
Toluhydroquinone	1·5	0·653
Trimethylhydroquinone	5·7	0·528
1:4-Naphthohydroquinone	40	0·482

Values of K calculated from (1) and quoted in Table I have been employed to calculate the chain-terminating efficiencies relative to that of hydroquinone. These are listed in Table II. Allowance has been made for the fact that whereas resorcinol and the 4 hydroquinones have two equivalent hydroxy groupings, the remainder have only one reactive group (in the case of pyrogallol reaction will presumably involve the 2-hydroxy group to the exclusion of the others).

The efficiency of an antioxidant is intimately related to its oxidisability and accordingly attempts have been made to correlate antioxidant efficiency with the oxidation-reduction potential of the antioxidant. Thus, Egloff, Lowry, Morrell and Dryer [3] examined the antioxidant effect of a wide range of phenolic and amino compounds on gasolene, and found

as a general trend, that antioxidant efficiency increased with diminishing oxidation-reduction potential. Elley[9] gives a set of figures relating the oxidation-reduction potential of a series of amines and aminophenols to their anti-ageing influence on vulcanised rubber, though details of the method of measurement and conditions of test are lacking. The antioxidant efficiency of the members of the series having critical oxidation-reduction potentials greater than 0·8 v. increase regularly with decreasing potential, but reduction of critical oxidation-reduction potential to 0·6 v. does not give any increase in efficiency, while those amines having still lower potentials are quite sharply less efficient.

The results of these authors, obtained as they are on systems where the precise role of the antioxidant cannot be determined, are subject to extraneous complications, such as the volatility and direct oxidation of the antioxidant; on the other hand we have here identified the chemical reaction from which antioxidant activity results (i.e. AH + RO_2—) and estimated the efficiency with which each of our series of phenols reacts in this particular way.

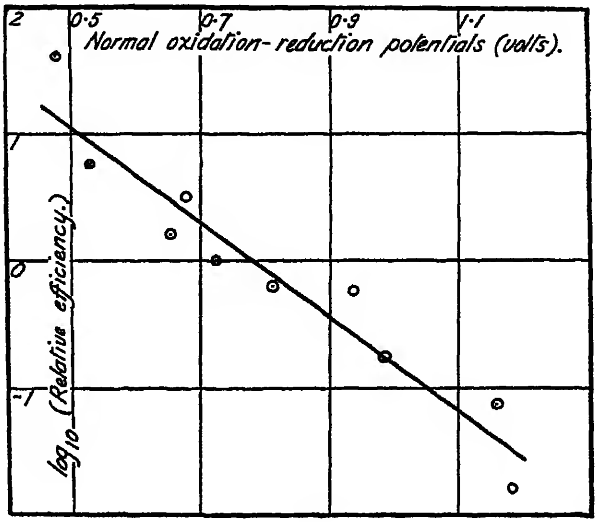


FIG. 1.

Now from Table II this efficiency increases progressively throughout the list of phenols arranged in order of diminishing normal oxidation-reduction potentials; the regularity of this correlation throughout the range of oxidation-reduction potentials 1·15 to 0·60 v. is apparent from Fig. 1 where a continuous plot is obtained between log (relative efficiency) and the normal oxidation-reduction potential, E_0.

The most obvious chemical interpretation of this quantitative dependence of antioxidant efficiency on the oxidisability of the antioxidant is that the termination reaction (R9) involves the transfer of a hydrogen atom from the antioxidant to the RO_2— radical, i.e.

$$AH + RO_2— \rightarrow ROOH + A—.$$

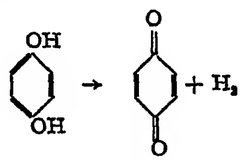
The efficiency of this reaction as we pass from one phenolic antioxidant to another would, because of its exchange character, be controlled entirely by the heat of reaction of the dissociation AH $\rightarrow$ A— + H—. In deciding whether normal oxidation-reduction potentials should in fact give a quantitative measure of the free energy change associated with the dissociation reaction (and, therefore, the heat of reaction since entropy changes will be little altered by the identity of AH) difficulties are encountered: in order to cover a sufficiently wide range of antioxidant efficiency it was necessary to study the effect of examples of two distinct types of phenolic compound which differ essentially in their electrochemical behaviour. Thus Table II includes 5 hydroquinones, which give completely reversible oxidation-reduction systems with well-defined

[9] Elley, *Trans. Electrochem. Soc.*, 1935, 69, 239.

quinones as the completely oxidised state, and also 5 phenols for which the normal oxidation-reduction potential cannot be determined directly owing to the incomplete reversibility of the redox systems. Conant and Fieser[15, 10, 16] have established that in the case of many phenols the following partly reversible system may be set up:

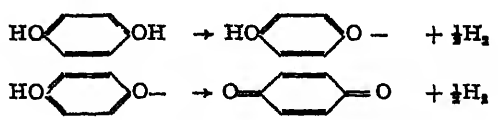
$$\begin{array}{c} AH + B \rightleftharpoons A + BH \\ \Big\downarrow \text{Slow} \\ \text{Final Products} \end{array}$$

where AH represents the phenol and B the oxidant of a suitable reversible oxidation-reduction system. They have introduced an experimental quantity, the "critical oxidation potential", which gives a relative measure of the free energy change in the reversible step—and therefore of the reaction $AH \rightarrow A— + H—$ —when the concentration of A is very small. Fieser[10] has suggested a method of deriving the hypothetical normal oxidation-reduction potentials for these systems from the critical oxidation potentials and this has been adopted in compiling Table II: such calculations involve uncertainties on at least three counts, and while little absolute accuracy may be claimed for these normal oxidation-reduction potentials, they should give a reliable measure of the relative ease of removal of the phenolic hydrogen atom from a series of phenols. Direct determination of the normal oxidation-reduction potential for the hydroquinone-quinone systems gives immediately the overall free energy change associated with the reaction, e.g.



ΔH

This in turn gives a relative measure of the corresponding heats of reaction (ΔH) for a series of hydroquinones if variations of entropy changes are neglected. There remains the problem of apportioning ΔH between the two successive steps



and

ΔH_1, ΔH_2

The relative values of ΔH, ΔH_1 and ΔH_2 within a series of hydroquinones will be determined by the differences in the resonance energies of the several hydroquinones, semiquinones and quinones, which may be represented by E_{HQ}, E_{SQ} and E_Q respectively. It may readily be shown that the necessary condition that ΔH_1 should decrease as ΔH decreases as we pass from one hydroquinone to another is that $\Delta E_Q > \Delta E_{HQ}$, $\Delta E_{SQ} > \Delta E_{HQ}$. If we consider a series of hydroquinones obtained by substitution of groups into the aromatic nucleus of the parent member, it becomes reasonable that such a relationship between ΔE_{HQ}, ΔE_{SQ} and

[10] Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 5204.
[11] Fieser and Peters, *ibid.*, 1931, **53**, 793.
[12] Conant and Fieser, *ibid.*, 1924, **46**, 1858.
[13] Conant and Fieser, *ibid.*, 1922, **44**, 2480.
[14] Conant, *Inter. Crit. Tables*, 1928, **6**, 333.
[15] Conant, *Chem. Rev.*, 1929, **3**, 1.
[16] See also Gershinowitz, *J. Chem. Physics*, 1936, **4**, 363.

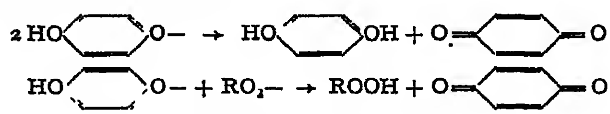
ΔE_Q should exist: the introduction for instance of an "acid-weakening" substituent (e.g. methyl) into an aromatic compound may be considered [17] to have the effect of increasing the importance of any ionic canonical forms which have a positive charge situated in the aromatic nucleus; conversely, canonical forms having negative charges in the aromatic nucleus are in this particular case of reduced importance. Since the ionic canonical forms of quinones are of the former type and those of the hydroquinones of the latter—with the semiquinones including examples of both types—it becomes likely that here $\Delta E_Q > \Delta E_{SQ} > \Delta E_{HQ}$. The condition that ΔH_1 should decrease with decrease in ΔH is thus apparently reasonable, and accordingly it may be expected that within series of hydroquinones which are all substitutive derivatives of one member, the oxidation-reduction potential will give a relative measure of the ease of removal of a phenolic hydrogen atom.* It is, however, to be noted that if such a series of hydroquinones is extended to include hydroquinones containing different aromatic nuclei it is no longer admissible to apply the above simple argument.

The regular manner in which chain-terminating efficiency increases with decrease in E_0 (cf. Table II) within each of the two series (*a*) of 5 phenols and (*b*) of the 3 hydroquinones, *p*-benzo-, tolu- and trimethylhydroquinone, leaves no doubt that termination reaction (R9) involves the rupture of the phenolic O—H bond according to

$$\dot{RO_2}— + AH \rightarrow ROOH + A—. \quad . \quad . \quad . \quad (R9)$$

Two earlier investigations provide chemical evidence that an antioxidant may react by loss of hydrogen atoms; Ziegler and Ewald [19] showed that the product resulting from the interaction between hexaphenyl ethane and oxygen was the disubstituted peroxide $(C_6H_5)_3C\,.\,OO\,.\,C(C_6H_5)_3$ while in presence of pyrogallol the sole product was the hydroperoxide $(C_6H_5)_3\,.\,COOH$ presumably formed by abstraction of a hydrogen from the pyrogallol by the peroxide radical $(C_6H_5)_3C\,.\,OO—$. Alyea and Bäckström [20] have demonstrated that alcohols which act as chain terminators in the oxidation of sodium sulphite are in the process converted to the corresponding aldehyde or ketone.

The essential requirement of the mechanism of inhibition by hydroquinone given earlier was the conversion of the chain carrier $RO_2—$, to stable non-radical products. In the light of the chemical formulation of the interaction between $RO_2—$ and AH now possible we may with some confidence suggest the following two ways in which the production of stable molecules may be completed:



[17] Branch and Calvin, *The Theory of Organic Chemistry* (New York, 1941).

* The work of Dimroth [18] is probably of interest in this connection. A study of the rate of dehydrogenation of certain dihydro compounds by different members of a series of *p*-benzoquinones showed that the rate of reaction increased smoothly with the normal oxidation-reduction potentials of the quinones, while in an example of the reverse type of reaction—between hydroquinones and hexanitroazobenzene—the rate diminished with increasing oxidation-reduction potential. While it is not possible to decide from Dimroth's data the identity of the rate-determining steps it is not unlikely that it involves in each case the formation of the semiquinone from the quinone or hydroquinone. On this assumption it follows that for substitution in *p*-benzoquinone

$$\Delta E_Q > \Delta E_{SQ} > \Delta E_{HQ}.$$

[18] Dimroth, *Z. angew. Chem.*, 1933, **46**, 571.

[19] Ziegler and Ewald, *Annalen*, 1933, **504**, 162.

[20] Alyea and Bäckström, *J. Amer. Chem. Soc.*, 1929, **51**, 90.

It is not possible to differentiate between these two possibilities on kinetic grounds. In the case of antioxidants where ready conversion to quinonoid forms is not possible, other reactions such as combination of A— radicals are probably important.

The mechanism of the antioxidant action of phenols described above centres round the competition between antioxidant and hydrocarbon molecules for the chain carrier, RO_2— according to (R9) or (R3) respectively. A consideration of the thermochemistry of these two reactions, based on the set of consistent bond energies already detailed [21] has led to the conclusion that for all examples of AH here concerned (*a*) reaction (R9) is—like (R3)—exothermic and (*b*) it is unlikely that reaction (R9) is in fact more exothermic than (R3). Now the two main factors which determine the energy of activation of exothermic reactions appears to be the heat of reaction and the degree of resonance stabilisation in the transition state and Evans and Warhurst [22, 23] have shown that in certain reactions at least the latter may be of predominant importance. It seems probable therefore that the deciding factor in making the energy of activation of (R9) smaller than that of (R3) is the resonance energy of the more highly symmetrical transition complex of reaction (R9) being greater than that associated with the transition complex of the competing reaction (R3).

Limiting Factors to Antioxidant Efficiency.

The dependence of the efficiency of the members of a series of phenolic antioxidants on the difference between the resonance energies of the A radical (E_{A-}) and the AH molecule (E_{AH}) should hold only over a limited range since at both low and high values of (E_{A-}—E_{AH}) additional complicating reactions would be expected to appear. Thus if (E_{A-}—E_{AH}) is sufficiently small the possibility arises that the reaction

$$A— + RH \rightarrow AH + R— \quad . \quad . \quad . \quad (R11)$$

would become important.

This reaction would obviously limit the efficiency of an antioxidant by replacing one oxidation chain carrier destroyed by reaction (R9) with another. Looking at it in a qualitative way, it is apparent that whether this reaction will actually be important hinges on whether the minimum value of (E_{A-}—E_{AH}) necessary for reaction (R9) to occur, is less than the maximum value of (E_{A-}—E_{AH}) consistent with the ready occurrence of reaction (R11). The most obvious kinetic consequence of the intrusion of (R11) is that the extrapolated oxidation chain length at infinite values of AH should be large. Measurements at high antioxidant concentrations (marked with asterisk in Table I) have been used to confirm that for all 9 phenols the extrapolated rates of oxidation at infinite [AH] correspond to chain lengths certainly not greater than 2. In the case of these phenols therefore reaction (R11) may be left out of account. It may be noted that reaction (R11) would be expected to be still less efficient in the case of other nonconjugated olefins, where the difference between E_{R-} and E_{RH} is invariably smaller. Preliminary examination of *p*-hydroxy-biphenyl as an antioxidant has, however, revealed that in the case of this particular phenol reaction, (R11) may be of importance, since here the oxidation chain-length extrapolated to infinite [AH] is as high as 17 (in presence of 2·2 moles benzoyl peroxide/mole ester at 45° c.).

A second limiting factor to the efficiency of an antioxidant should appear when (E_{A-}—E_{AH}) becomes sufficiently great: owing to the re-

[21] Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 244.
[22] Evans and Warhurst, *ibid.*, 1938, **34**, 614.
[23] Evans, *ibid.*, 1939, **35**, 824.

sulting ease of dehydrogenation, molecular oxygen itself may attack the antioxidant, presumably according to

$$AH + O_2 \rightarrow HO_2— + A—.$$

Our series of phenols has been extended to include examples of sufficiently low oxidation-reduction potential for this effect to be appreciable.

Readily-oxidisable Phenols as Antioxidants.

Egloff, Lowry, Morrell and Dryer [2] have drawn attention to the possibility that antioxidants of sufficiently low oxidation-reduction potential may themselves interact directly with oxygen under the test conditions. Induction periods measured under such circumstances naturally fail to reflect the chain-terminating efficiency of the antioxidants. Doubtless this is the explanation of the apparently poor antioxidant properties observed by Elley for amino-compounds of critical oxidation potential less than 0·6 v. Under the mild temperature conditions used above the direct oxidation of hydroquinone was not appreciable, judging from the fact that the rate of removal of hydroquinone from the oxidising linoleate was independent of oxygen pressure: when, however, trimethyl-hydroquinone (E_0 = 0·528 v.) and 1 : 4-naphthohydroquinone (E_0 = 0·482 v.) were used as antioxidants, indications were obtained that their oxidisability was sufficiently great to complicate matters.

TABLE III.

Antioxidant.	[AH]. (moles/mole ester) $\times 10^4$.	[ROOH]. (moles/mole ester) $\times 10^2$.	p. (mm.)	R_U. (moles O_2/mole ester/min.) $\times 10^{-4}$.	R_s. (moles O_2/mole ester/min.) $\times 10^{-4}$.	t_{∞}. (min.)
1 : 4-Naphtho-hydroquinone	0·76	17·7	10	2·30	0·006	100
	0·77	17·7	25	2·30	0·005	50
	0·80	17·7	50	2·30	0·005	32
Hydroquinone .	0·80	17·7	50	2·30	0·210	105

In the first place these two hydroquinones react with dibenzoyl peroxide *in vacuo* with the result that their concentration in the reaction mixture was diminished to an appreciable extent during the necessary period of evacuation prior to the introduction of oxygen into the apparatus. When, however, ethyl linoleate hydroperoxide is substituted for dibenzoyl peroxide as chain initiator this difficulty is removed. Accordingly in carrying out the comparison of the antioxidant efficiency of trimethylhydroquinone and 1 : 4-naphthohydroquinone with that of hydroquinone their retarding effect on the rate of oxidation of ethyl linoleate containing 1·7 % peroxidic oxygen has been determined. The results of 3 such experiments with 1 : 4-naphthohydroquinone are summarised in Table III. The times required for complete removal of antioxidant quoted (t_{∞}) are estimated from the time taken for the rate of oxidation to reach its original uninhibited rate, and undoubtedly are liable to some uncertainty. For comparison, the time required for the removal of hydroquinone under rather similar experimental conditions is included. These figures demonstrate (*a*) that the 1 : 4-naphthohydroquinone is removed from the system more rapidly than hydroquinone, and (*b*) that in contrast to hydroquinone, the rate of removal definitely increases with increase in oxygen pressure. It is difficult to escape the conclusion that the antioxidant is itself destroyed by direct interaction with oxygen.

It has not been found practicable to measure the initial rates of oxidation over a wide range of 1 : 4-naphthohydroquinone concentration: at concentrations lower than those detailed in Table IV the rate of oxidation increases sufficiently rapidly with time to make extrapolation to zero time uncertain. The initial rates of oxidation observed with only $0{\cdot}8 \times 10^{-4}$ mole 1 : 4-naphthohydroquinone/mole ester correspond to only a fractional chain length and are some 40 times smaller than the rate of oxidation in presence of the same concentration of hydroquinone. The estimate of the relative chain-terminating efficiency of 1 : 4-naphthohydroquinone based on the ratio and quoted in Table II must be treated as approximate, since when the apparent chain length of oxidation is of the order of unity its reliability must be questioned as secondary effects, such as the evolution of volatile products may be of comparable magnitude to the rate of oxygen uptake.

The authors wish to express their thanks to Dr. G. Gee for his interest and advice during this work which forms part of the programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

Summary.

The effect of 10 phenolic antioxidants on the oxidation of ethyl linoleate has been investigated and the efficiencies with which they bring about the termination of the oxidation chains (by interacting with the peroxide-radical chain-carrier, RO_2-) compared. The chain-terminating efficiency is shown to increase with decreasing oxidation-reduction potential (i.e. increasing oxidisability) of the antioxidant within two series of phenolic compounds, leading to the conclusion that the chain-termination reaction is $RO_2^- + AH \rightarrow ROOH + A$— (where AH represents the phenol).

It is demonstrated that in the case of a sufficiently oxidisable phenol (normal oxidation-reduction potential < *ca.* 0·6 v.) destruction by direct reaction with oxygen becomes the most important factor in determining its practical utility as an antioxidant.

Résumé.

L'effet de 40 antioxydants phénoliques sur l'oxydation du linoléate d'éthyle a été étudié et leurs capacités respectives pour terminer les chaînes d'oxydation, comparées. Cette propriété augmente avec des potentiels d'oxydo-réduction croissants de l'antioxydant, pour deux séries de composés phénoliques, suggérant ainsi que la réaction de terminaison de chaîne est :

$$RO + AH \rightarrow ROOH + A \text{ (où AH = phénol).}$$

Quand le potentiel d'oxydo-réduction du phénol est inférieur à 0·6 v., le facteur dominant est la destruction par réaction directe avec l'oxygène.

Zusammenfassung.

Die Wirkung von 10 phenolischen Antioxydanten auf die Oxydation von Äthyllinoleat wurde untersucht und ihre Wirksamkeit für den Abbruch von Oxydationsketten verglichen. Diese Wirksamkeit wächst mit zuwachsendem Redoxpotential des Antioxydanten innerhalb von zwei Reihen von Phenolverbindungenan, was darauf hindeutet, dass der Kettenabbruch

$$RO_2 + AH \longrightarrow ROOH + A \text{ (AH = Phenol)}$$

ist. Wenn das Redoxpotential des Phenols geringer als 0·6 v. ist, wird die Zerstörung durch direkte Reaktion mit Sauerstoff der vorherrschende Faktor.

GENERAL DISCUSSION

Dr. M. J. S. Dewar (*Maidenhead*) said : The point raised by Dr. Birch concerning the different modes of addition of reagents with differing reactivity to mesomeric systems is clearly of very great importance. His interpretation can be amplified somewhat as follows.

Let us consider a definite example, the addition of a cation X^+ to the pentadienate anion (I)

$$(\overset{1}{C}H_2 \cdots \overset{2}{C}H \cdots \overset{3}{C}H \cdots \overset{4}{C}H \cdots \overset{5}{C}H_2)^- \qquad CH_2{=}CH{-}CH{-}CH{=}CH_2 \qquad \overset{-}{C}H_2{-}CH \cdots CH \cdots CH \cdots CH_2.$$

(I) (II) (III)

Quantum mechanical calculation shows that in (I) the negative potential is greatest at C_3. Therefore collisions of X^+ with C_3 will be more frequent than with the other carbon atoms. The collision frequency for addition of X^+ to C_3 will therefore be greater than for terminal addition.

The activation energies of the two reactions will, however, differ, since terminal addition gives a mesomeric butadiene derivative, central addition an unconjugated 1 : 4-pentadiene. The energy relationships are shown roughly in the figure, where the configuration of the system is represented in terms of a suitable " reaction-co-ordinate," giving a section of the energy surface. Curve A represents the conversion of (I) to the unconjugated anion (II), where an electron pair is localised on C_3 ; curve B likewise the conversion of (I) to (III). Curve X_1 represents the fission of $CH_2{=}CH{-}CHX.CH{=}CH_2$ (IV) to X^+ and (II) and curve X_2 the fission of $CH_2{=}CH.CH{=}CH.CH_2X$ (V) to X^+ and (III). Thus the reaction of (I) with X^+ to give (IV) is represented by the line CDE, and its activation energy by the difference in ordinates between C and D ; and reaction to give (V) by CFG, and the activation energy by the difference in ordinates between D and F. The curves Y_1, Y_2 represent likewise the reactions of a more active cation Y^+ (i.e. one which reacts more exothermically with (I)). It is evident from the geometry of the figure that formation of C_3 adducts (e.g. (IV)) will have a higher activation energy than formation of C_1 adducts (e.g. (V)), but that the activation energy difference will decrease as the activity of the reagent increases.

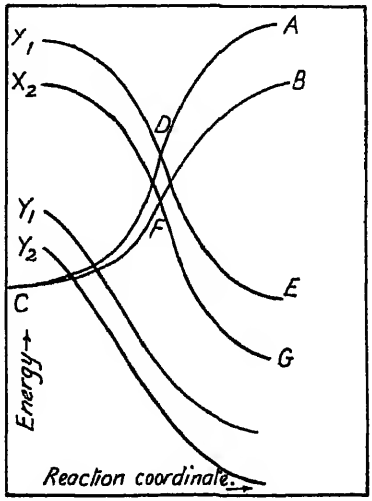


FIG. 1.

Hence it may well happen that for reagents of high activity, the activation energy difference is negligible, and the higher collision frequency leads to C_3 addition ; while in less active reagents the activation energy difference leads to addition at C_1. This interpretation accords well with the effect of temperature on the mode of addition of inactive reagents, summarised by Dr. Birch.

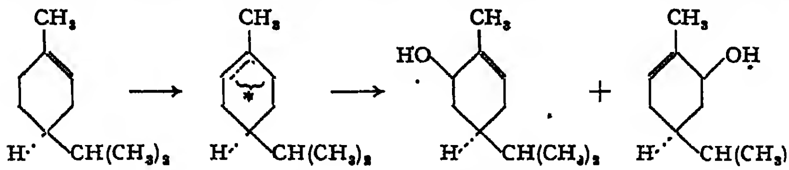
This argument, applied in a specific case, is clearly of general utility. The relative collision frequencies for different modes of addition to a mesomeric molecule may be affected not only by charge-charge or charge-dipole attractions, but also by differences in entropies of activation ; while the modes of reaction may be distinguished energetically not only

by resonance energy differences, but also by bond-energy or electron-affinity differences. Thus in addition of cations to enolate ions, C-addition is energetically favoured since the ketone has a higher bond-energy sum than the corresponding enol, but since the charge in the enolate ion resides mainly on the oxygen, highly active cations (H^+, acylpyridinium) attack oxygen to give enolic derivatives.

Dr. A. J. Birch (*Oxford*) (*communicated*) : I should like to agree with this interpretation of Dr. Dewar. I believe the ideas to be generally valid for mesomeric anions, cations or radicals, and hope to discuss them in more detail elsewhere. I have chosen anions for illustrative purposes because they happen to be most easily dealt with in the present state of knowledge.

Dr. W. A. Waters (*Oxford*) said : Our studies in Oxford of oxidations with chromic acid support Prof. Fieser's conclusion that oxygen uptake occurs only as a minor side-reaction. It seems that if free hydrocarbon radicals are formed then they must be attacked much more rapidly by CrO_3 than by oxygen. However, the initial point of attack on Prof. Fieser's complex molecules often seems to be the point at which a radical would attack a hydrocarbon chain.

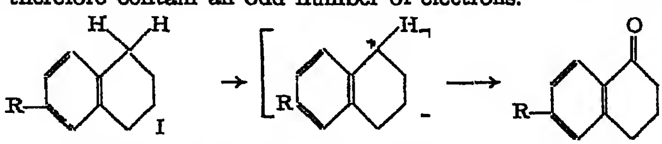
Dr. A. J. Birch (*Oxford*) said: The description of a number of reactions in solution as " free-radical " is doubtful in that the radicals may sometimes be far from " free ", but it can be used as an indication that in these cases transition states occur involving the transfer of an odd number of electrons. This seems to be so for " substitutive " oxidations by means of selenium dioxide, oxygen or chromic acid. Evidence for the formation of mesomeric intermediates can be gained from reactions like the oxidation of 4-methylcyclohexene-1.[1] In this the three possible products obtained by addition of oxygen to both ends of the two possible mesomeric systems are obtained (cf. also [2]). That such systems are sometimes not completely " free " is shown by the formation of the partially, but *not completely*, racemised products from optically active *p*-methene-1.[3, 4]



(Predominant)

From known stereochemical relations it can be shown that the direction of rotation of the product corresponds to major addition of oxygen at the site of the original CH_3 group.

It is clear that in such cases the mesomeric system is not anionic, since the most acidic hydrogen is not the one removed. In the oxidation of (I, R=OCH_3 or NO_2) to (II, R=OCH_3 or NO_2) [5, 6] reaction in both cases takes place *para* to the substituent, indicating that the initial transition state is stabilised by either an electron-absorbing or -donating group. It must therefore contain an odd number of electrons.



[1] Guillemonat, *Ann. Chim.*, 1939, 11, 143.
[2] Farmer, Koch and Sutton, *J. Chem. Soc.*, 1943, 541.
[3] Tabuteau, *Compt. rend.*, 1935, 200, 244.
[4] Blumann and Zeitschel, *Ber.*, 1914, 47, 2623.
[5] Burnop, Elliott and Linstead, *J. Chem. Soc.*, 1940, 730.
[6] v. Braun, *Annalen*, 1927, 461, 40.

Dr. W. A. Waters (*Oxford*) said: The results of Dr. Bolland and Dr. ten Have give us a most valuable substantiation of the view that in liquid-phase autoxidation processes the radical R—O—O• is present in much higher concentrations than the hydrocarbon radical R•, it is the chemical properties of R—O—O• radicals which are significant in chain termination. This work supports conclusions reached by Dr. A. Robertson and myself [7] from the study of the autoxidation of tetralin, in which under conditions in which the chain-starting radicals are derived from the thermal breakdown of tetralin hydroperoxide, the chain terminating process seems to be $R—O—O^{\bullet} + {}^{\bullet}OH \rightarrow R—OH + O_2$, and *not* $R^{\bullet} + {}^{\bullet}OH \rightarrow R—OH$. Perhaps the reaction $H—O—O^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2$ should be included similarly, as one of the chain-terminating reactions involved in the full scheme of the catalase decomposition of hydrogen peroxide.

[7] *J. Chem. Soc.* (in press).

D.—EXPERIMENTAL TECHNIQUE.

AN EXPERIMENTAL METHOD FOR USE IN CHEMICAL KINETICS AND IN THE STUDY OF TRANSIENT INTERMEDIATES.

By Brenda Stead, F. M. Page and K. G. Denbigh.

Received 6th August, 1947.

The method of investigating chemical kinetics by the streaming of the reactants through a tube has been used extensively, and especially in the hands of Hartridge and Roughton, in the study of very rapid reactions. The advantage of the method is the attainment of a time-invariant state. The change in composition due to reaction is transferred to a space co-ordinate—the direction of flow—in place of the variation in time which occurs in the batch or static system.

The type of continuous flow method described below does not seem to have been used previously in kinetic work, although it has a widespread use in chemical industry. It differs essentially from the technique of Hartridge and Roughton in that the reaction space is a well-stirred chamber instead of a tube. The reaction system again approaches a stationary state, but it is uniform in composition throughout its volume, and does not vary from point to point, as in the streaming method.

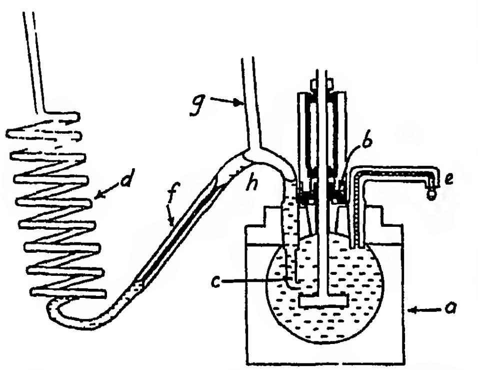
The reactant solutions are fed separately and continuously into a vessel which has appreciable volume and is thoroughly stirred. Reaction takes place in the vessel and the product, together with unchanged reactants, are steadily discharged through an overflow. By the achievement of very efficient mixing, the composition is made uniform throughout the liquid phase and equal to that of the solution which passes out of the vessel through the overflow. When the steady state is attained, an instantaneous analysis of the liquid in the vessel therefore corresponds to concentrations which are both stationary and uniform. The method thus combines some of the advantages of both streaming and static methods. Its essential requirement is that of flow through a well-stirred *capacity*. The term capacity flow may be used, to distinguish it from the streaming or tube flow method of Hartridge and Roughton. The theory of capacity-flow systems has been discussed previously by one of the authors.[1]

[1] Denbigh, *Trans. Faraday Soc.*, 1944, 40, 352.

As an experimental technique the method seems likely to be of particular value in the study of complex reactions. For example, the concentration of a transient intermediate can be held constant in the reaction vessel over an extended period of time, whereas in a static system its formation and decomposition might be complete in a period too short for investigation. The details of experimental procedure have been carefully studied and, in particular, the conditions necessary to achieve constancy of the flow rates and a high degree of mixing. The present paper describes this work and also the testing of the accuracy of the method on a familiar reaction, the hydrolysis of ethyl acetate. Its field of usefulness in chemical kinetics is discussed in the concluding section.

Experimental.

Apparatus.—The main features of the apparatus, as finally developed, are shown in the figure. The reaction vessel, (*a*), of about 400 cc. capacity, was machined out of solid Perspex and is in the form of a short horizontal cylinder. The two ends of the cylinder consist of plane Perspex windows for use in the optical investigation of reaction intermediates. The vessel is stirred by means of a synchronous motor at 3000 R.P.M. and is supported in a thermostat. The reaction vessel in use is completely full of liquid, i.e. is without an air-liquid interface. The reasons for this are twofold. In the first place, the presence of an interface gives rise to the development of waves and this causes irregularity in the outflow from the vessel. Secondly, the presence of a vortex causes uncertainty as to the true volume of the reaction space.



Much difficulty has been experienced in preventing the inlet of air as it tends to creep down the stirrer shaft. This leakage was finally prevented by the use of a centrifugal liquid seal (*b*). This consists of a small disc which is fixed to the shaft and rotates inside a cavity in the casing. A small amount of water placed in this cavity is acted on by the centrifugal force and is thrown outwards so that it forms a seal between the disc and the wall of the casing. This part of the apparatus and the stirrer were also made of Perspex, apart from a pair of ball bearings above the seal.

The reactants are contained in two large aspirators (not shown in the diagram) and which operate as Mariotte bottles. Each reactant is fed separately into the reaction vessel at two inlet points, (*c*), only one of which is shown. The reactants are warmed to the temperature of the bath by passing through submerged coils, (*d*), each of which consists of about 130 cm. of thin-walled glass tubing. The solution passes out of the reaction vessel through the capillary overflow (*e*) and is run to drain, except during the taking of samples.

The rate of flow of the reactants is controlled by the capillaries (*f*) on each of the inflow pipes. In order to avoid syphoning, the capillaries are followed by the side arms (*g*) which communicate with the atmosphere. The rates of flow through the capillaries are thus determined by the constant difference in level of the solutions at two points which are both at atmospheric pressure—i.e. the point of inlet of air into the Mariotte bottles and the point (*h*) above the capillaries. The driving force is thus independent of momentary fluctuations of pressure in the reaction vessel. Even so, great difficulty was experienced in maintaining a sufficient degree of constancy in the rates of flow. This was traced to small variations in the viscosity of the solutions in the length of tube between the aspirators and the heating coils. The laboratory was therefore held at a constant temperature and it was found possible to reduce the fluctuations in flow rate to 0·2 % or less, over periods of several hours' running of the apparatus.

Efficiency of Mixing.—As described above, the theory of the method depends on the attainment of a high degree of homogeneity of the liquor in the reaction

vessel. The inflowing molecules of reactant must therefore be dispersed throughout the vessel in a time which is very short compared to the mean time of passage. Experimental work on the efficiency of mixing with various types of stirrer was carried out by a method depending on the rate of decolourisation of the starch-iodine complex. The addition to the blue solution of one drop of N./10 thiosulphate was sufficient to cause discharge of the colour and the time required for this process was measured. The stirrers which were examined consisted of

TABLE I.

Stirrer Blade, 3·8 cm. Diameter.	Area * cm.².	Time for Discharge of Colour, Seconds.				
		130 R.P.M.	160 R.P.M.	195 R.P.M.	265 R.P.M.	369 R.P.M.
30° propellor	1·1	15·7	8·8	7·6	5·5	2·1
60° ,,	1·4	10·9	7·8	5·8	3·4	1·5
Paddle, 0·64 cm. wide	2·5	7·4	5·2	3·8	2·5	1·3
,, 0·95 ,,	3·6	5·6	4·6	3·6	2·0	0·9
,, 1·27 ,,	4·9	5·0	3·8	3·0	1·7	0·7
,, 1·59 ,,	6·1	3·8	3·0	2·6	1·4	—

* The area quoted is that of the projection perpendicular to the plane of rotation.

propellors, twisted at angles of 30° and 60°, and flat paddles of various areas. It was found that the propellors were not more efficient than the flat paddles and it appears, in fact, that the most important dimension of the stirrer blade is the area which it exposes in the plane perpendicular to the plane of rotation.[2]

The experimental results are shown in Table I and on the basis of this work it was decided to use a flat paddle stirrer 3·8 cm. from tip to tip and 1 cm. wide. The speed of rotation of this stirrer in the reaction vessel is 3000 R.P.M. A rough extrapolation to this speed of the results of Table I indicates that dispersion of reagent in the reaction space should be substantially complete in much less than a tenth of a second.

TABLE II

Time, Min.	Relative Concentration in Outflow.	
	Theoretical.	Observed.
0	0	0
3·3	0·101	0·098
9·3	0·259	0·261
20·3	0·480	0·478
37·3	0·699	0·694
66·3	0·882	0·879
75·3	0·911	0·908
93·3	0·950	0·950
119·3	0·978	0·978
178·3	0·997	0·993
248·3	0·999	0·999

The experiments on mixing described above were carried out under static conditions—i.e. of zero flow through the vessel. It was desirable to confirm the existence of good mixing under the actual conditions of flow as used in the continuous reaction apparatus as previously described. The method which was adopted depended essentially on the statistical distribution among the individual molecules of the time of passage through the reaction vessel. The law of this effect is easily derived,[1, 3] and can be compared with experiment as a test of good mixing.

The experiment and its theory are as follows. Starting with the reaction vessel full of water, at a particular moment, $t = 0$, a continuous flow of dilute NaOH solution was introduced into it from one of the Mariotte bottles. Samples of the outflow from the reaction vessel were collected at intervals of time up to $t = 4\frac{1}{2}$ hr., and were subsequently weighed and titrated. Now if the incoming NaOH solution had taken a particular chosen route across the reaction vessel,

[2] Similar conclusions are reached by Asquith, *Chem. Trade J.*, 1945, 116, 107. Also White and Summerford, *Chem. Met. Eng.*, 1936, 43, 370; and Hixson, *Ind. Eng. Chem.*, 1944, 36, 488.

[3] McMullin and Weber, *Trans. Amer. Inst. Chem. Eng.*, 1935, 31, 409.

from inlet to outlet, the attainment of a concentration in the outflow equal to that in the inflow would clearly have been very rapid. On the other hand, if mixing were perfect, the final concentration would be approached asymptotically, by the progressive " dilution " of the residual water in the vessel by the inflowing NaOH solution. The appropriate law is obtained as follows. Let u be the volumetric rate of flow of solution and x_0 be the concentration of alkali in the Mariotte bottle. The constant rate of inflow of alkali is therefore ux_0 (moles/sec.). At a particular moment, t, let the measured concentration in the outflow be x so that the corresponding rate of outflow is ux. It follows that at this moment alkali is accumulating in the vessel at the rate $(ux_0 - ux)$ (moles/sec.), or at a rate $u(x_0 - x)/V$ per unit volume, where V is the volume of solution in the vessel. This is therefore the rate of increase of the internal concentration. According to the hypothesis of perfect mixing this concentration is uniform and is equal to x, the concentration in the outflow.

Hence
$$\frac{dx}{dt} = \frac{u}{V}(x_0 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\therefore \log_e \frac{x_0}{x_0 - x} = ut/V,$$

or
$$\log_e (1 - r) = -ut/V, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $r = x/x_0$, is the concentration in the outflow as a fraction of the inflow concentration.

The theoretical values of r, as calculated from eqn. (3), are shown in the second column of Table II. and are in very good agreement with the experimental figures as shown in the third column.

The reaction vessel in use in these experiments was not the cylindrical vessel described above, but was a spherical Pyrex vessel used in work on the rate of hydrolysis of ethyl acetate. This vessel had three flattened regions on its walls in order to prevent the liquid from rotating as a mass and thus to facilitate the mixing. The free volume was 602 cc. and the rate of flow of alkali solution was 19·4 cc./min. The nominal time of passage was thus $602/19{\cdot}4 = 31{\cdot}1$ min. Examination of Table II shows that the system was within about 0·1 % of the final steady state after 4 hr. running—i.e. after a period of time about 8 times greater than the time of passage.

Test of the Method by Measurement of the Rate of Hydrolysis of Ethyl Acetate.

It was desirable to test the suitability of the method for the measurement of velocity constants and for this purpose the authors investigated the alkaline hydrolysis of ethyl acetate. A solution of re-purified A.R. ethyl acetate was contained in one of the Mariotte bottles and a solution of CO_2-free alkali was contained in the other. All air entering the Mariotte bottles was freed from CO_2, as was also the air in contact with the solutions at the " breathing " points, (g), in the diagram.

The reaction vessel which was used in these experiments was the spherical Pyrex vessel described in the previous section. At the commencement of each experiment the vessel contained distilled water only. This was gradually displaced by the flow of the two reactants and the progress of this displacement was followed by rough titrations of the out-flowing liquor. After several hours running of the apparatus, when it was evident that the composition had attained constancy, a number of careful analyses were made of the liquor leaving the capillary overflow. For this purpose, samples of the liquor were collected in weighed Pyrex flasks which contained a very small excess of N./100 HCl, in order to stop the reaction (hydrolysis by acid is much slower than by alkali). During the collection of each sample a slow stream of CO_2-free air was passed through the flasks. These samples were quickly weighed and back-titrated with baryta until neutral to cresol-red. Weight titrations were used throughout. Finally, when several such analyses had been made and were in agreement, the rate of flow of the reaction liquor was determined by collection and weighing of samples over measured periods of time. The flow rate of each reactant was also measured separately.

Let x_0 and y_0 be the normality of alkali and of ethyl acetate respectively in the Mariotte bottles and let x and y be their normality in the reaction vessel at a particular moment t. Let u_x and u_y be the flow rates (l./sec.) of the alkali

and ethyl acetate solutions respectively. Provided there is no volume change in the reaction, $u_x + u_y = u$, where u is the rate of outflow from the reaction vessel. The constant rate of entry of hydroxyl ion into the reaction vessel is thus $u_x x_0$ (g. ions/sec.). It is removed simultaneously by the two processes of chemical reaction and of mass-transport in the outflowing solution. The rate of the latter process, at the moment t, is ux (g. ions/sec.). The rate of the chemical process is kxy g. ions of hydroxyl destroyed per sec. in each litre of reaction space. In the whole volume, V, of the reaction space the rate of reaction is thus $Vkxy$ (g. ions/sec.). The rate of accumulation of hydroxyl ion in the vessel is thus $u_x x_0 - ux - Vkxy$. Dividing through by V, we obtain the rate of increase of concentration:

$$\frac{dx}{dt} = (u_x x_0 - ux)/V - kxy. \qquad (3)$$

(cf. eqn. (1)).

As the system approaches the steady state the differential becomes negligibly small and hence in the limit

$$(u_x x_0 - ux)/V - kxy = 0. \qquad (4)$$

The corresponding mass balance equation for ethyl acetate is:

$$(u_y y_0 - uy)/V - kxy = 0. \qquad (5)$$

The elimination of y between these equations gives the following expression for the velocity constant, k:

$$k = \frac{u(u_x x_0 - ux)}{Vx(u_y y_0 - u_x x_0 + ux)}. \qquad (6)$$

The capacity-flow system, at the steady state, thus allows of the evaluation of k by use of a simple equation which does not require to be integrated. The importance of this point in the study of complex reactions will be discussed in the concluding section.

For the purpose of analysing the errors in the method, equation (6) can be simplified by writing, as an approximation, $u_x = u_y = u/2$. The equation then reduces to:

$$k = \frac{u(x_0 - 2x)}{Vx(y_0 - x_0 + 2x)}$$

Errors in u and V clearly give rise to equal percentage errors in k. From the partial derivatives it is found that errors in x_0, y_0 and x give rise to rather larger errors in k; however, by suitable choice of the variables the factor can be made not to exceed 2.

TABLE III.

Alkali.	Normality of Feed Solutions.		Flow Rates, l./sec.		Steady State System.		$k \times 10^3$ l./g. mole./sec.
	Alkali, $x_0 \times 10^2$.	EtAc, $y_0 \times 10^2$.	$u_x \times 10^4$.	$u_y \times 10^4$.	$x \times 10^2$.	Ionic Strength.	
NaOH .	1·208	4·62	3·12	3·14	0·198	0·0060	11·0
$Ba(OH)_2$	0·511	3·94	3·18	3·32	0·0917	0·0038	10·1
,, .	0·587	3·89	3·22	3·32	0·1094	0·0043	9·9
,, .	0·767	3·88	2·91	3·34	0·1268	0·0053	10·2
,, .	0·965	10·40	3·18	3·33	0·0866	0·0071	9·8

The results of five determinations of k at 25·0° C. are given in Table III. The first of these was obtained using caustic soda as the alkali and the value for k, $11·0 \times 10^{-3}$, is in good agreement with the value of $10·8 \times 10^{-3}$ which was obtained in the classical researches of Reicher,[4] Warder[5] and Walker.[6]

[4] Reicher, *Annalen*, 1885, **228**, 257; 1885, **232**, 103.
[5] Warder, *Amer. Chem. J.*, 1881, **3**, 340.
[6] Walker, *Proc. Roy. Soc. A*, 1906, **78**, 157.

For the remainder of the measurements it was found more convenient to use baryta and the mean value of the results is $10{\cdot}0 \times 10^{-8}$, which is 8 °/₀ lower than for NaOH. This value cannot be compared immediately with the literature as there has been no accurate measurement with baryta at the same temperature. However, in his detailed comparison of various bases at 9·4° c., Reicher found k for baryta to be 7 °/₀ lower than for NaOH. It is concluded that the capacity-flow method will give velocity constants which are correct to within 1-2 °/₀.

Applications of the Method.

From the work described it may be concluded that the method is suitable for use in reaction kinetics and is capable of further refinement. The only important limitations to its use are: (*a*) fairly large quantities of reagents are required; (*b*) the procedure is rather slow. Thus each experiment gives only a single item of information and not a number, as when a series of measurements are made during the course of a run by the static method. The method is thus not very suitable for exploratory work on a reaction of unknown mechanism. Its main value will be found in cases where the classical methods are difficult in application and where special use can be made of its essential properties. These depend on the attainment of a steady state and on the fact that reaction takes place in a system of uniform concentration which is diluted by its own reaction product. In place of a continuous change of composition there is a stepwise change between the composition of the inflowing reactants and of the reaction system itself. The latter is both constant in time and uniform in space. There is always, of course, a proportion of unchanged reactants in the outflow from the vessel. Loss of reactants is only avoided by using a number of such vessels in series, so that there is a stepwise change in composition from one to the next. In kinetic studies this incompleteness of reaction is not important.

The uses of the method, as they appear at present, may be summarised as follows.

(*a*) Reaction can be studied under entirely constant conditions, for example, of catalyst or free-radical concentration, or of ionic strength,* and at any chosen stage of the reaction process.

(*b*) Mathematical analysis of the reaction kinetics can be carried through in cases which are intractable when reaction is carried out in a static system.

(*c*) The method can be used for the measurement of reaction rates which are too fast for investigation by a static method but which are too slow for convenient application of the Hartridge and Roughton technique.

(*d*) The method allows of the investigation, by physical methods, of transient reaction intermediates.

With regard to the second point above, it is to be noted that the steady state requires only algebraic equations for its description, as has been shown for the simple case of ethyl acetate hydrolysis. In a static system, on the other hand, there is a process of continuous change and this requires for its description the use of differentials. (The same applies also to the case of flow through a tube.) In the case of simple reactions the differential equations of a static system are, of course, easy to solve and the present method offers no advantage. Considerable mathematical advantage is obtained, however, in the case of complex reactions, especially those consisting of successive steps, such as the saponification of polyesters. This point will be developed in a forthcoming publication on the

* Variation of ionic strength, during the course of a reaction in a static system, presents a serious difficulty in the interpretation of results, as Scatchard [7] has shown. The authors are indebted to Dr. Moelwyn-Hughes for pointing out the advantages of the continuous reaction system, in this respect.

[7] Scatchard, *J. Amer. Chem. Soc.*, 1930, **52**, 52.

theory of continuous polymerisation, where it is shown that the mathematical analysis can be carried much further than is possible for a static system.

An interesting application is the study of labile molecules, especially when the formation and breakdown are too rapid for measurement by the usual methods. An example which is being studied at present is the complex formed during the reaction of ferric salts and sodium thiosulphate. When solutions of these reagents are mixed a violet-coloured substance is immediately formed and disappears again within 1-2 min. Its formula has been variously reported as $FeS_2O_3^+$, $Fe_2(S_2O_3)_3$ and $Fe(S_2O_3)_2^-$. The difficulty which is experienced in the study of this complex by traditional methods is the speed of its breakdown, except under conditions of very high dilution or of low temperature.[8] The reaction is also greatly catalysed by traces of cupric ions.

In the present work solutions of the two reagents are fed continuously into the reaction vessel, as described above. After some hours' running the concentration of the complex reaches a stationary value and at this stage the colour intensity is measured by passing through the reaction vessel a beam of monochromatic light which is received on a photocell. The absorption coefficient of the complex is, of course, unknown, but from the extent of the light-absorption it is possible to obtain relative values of the concentration of the complex in different experiments. These relative values can then be related to the corresponding stationary concentrations of the reagents. These concentrations are determined by taking samples of the outflow from the reaction vessel and rapidly quenching the reaction in a phosphate-acetate solution, followed by iodimetric titration.

The work is not yet sufficiently far advanced to be reported in detail. The example shows, however, how it is possible to maintain a uniform concentration of a labile molecule and in a volume of sufficient thickness for the application of optical methods. The usefulness of the type of flow system which has been described will largely depend on such applications of its special properties of spatial and temporal invariance.

In conclusion we wish to express our indebtedness to Mr. W. T. Moore, and the engineering staff of this laboratory, for assistance in the construction of apparatus.

Note added in proof. Dr. Szwarc has pointed out to the authors that Bodenstein and Wolgast (*Z. physik. Chem.*, 1908, **61**, 422) have previously considered a rather similar type of continuous flow-system in which there is approximate homogeneity throughout a reaction vessel due to diffusion being assumed more rapid than chemical reaction. Bodenstein and Wolgast do not apply high speed stirring as in the present method.

Summary.

The paper describes a new experimental method for use in chemical kinetics. In principle it depends on the setting-up of uniform and stationary concentrations in a well-stirred vessel through which there is a continuous flow of the reagents. The method is well adapted to the examination, by physical methods, of labile reaction intermediates.

Résumé.

Cet article décrit une nouvelle méthode expérimentale, qu'on peut employer en cinétique chimique. En principe, elle dépend de l'établissement de concentrarions uniformes et stationnaires dan un milieu bien agité, dans lequel on fait passer un courant continu des réactifs. Elle est bien adaptéé à l'étude, par des méthodes physiques, des intermédiaires labiles des réactions.

[8] Uri, *J. Chem. Soc.*, 1947, 335.

Zusammenfassung.

Der Artikel beschreibt eine neue experimentelle Methode zur Anwendung in der chemischen Kinetik. Prinzipiell besteht diese darin, dass man in einem gut gerührten Gefäss, durch das die Reagenzien fortwährend fliessen, einheitliche und stationäre Konzentrationen aufrechterhält. Die Methode eignet sich gut zur Untersuchung von labilen Reaktionszwischenprodukten auf physikalischem Wege.

Imperial Chemical Industries Ltd.,
Butterwick Research Laboratories,
The Frythe,
Welwyn, Herts.

GENERAL DISCUSSION.

Dr. W. A. Waters (*Oxford*) said: In summarising the trend of the discussion I would say that it has been made quite obvious that we are concerned with a subject of very active scientific interest, in which, as yet, we are able to put forward more speculative theories than conclusions which we have been able to confirm experimentally. The reactions of free hydroxyl have concerned us greatly, but we have had a most valuable reminder from Dr. Minkoff that we should not attempt to explain all the reactions of hydrogen peroxide and its analogues by means of free radicals. Dr. Dewar too has stressed the point that we cannot yet be sure of the free-radical mechanism for all cases of glycol splitting.

The discussion of Dr. Bawn's paper indicated to us that free methyl and free phenyl might have appreciably different chemical properties, and we have had hints that in the decompositions of the metallic alkyls, at least, the actual process of bond rupture was not quite clear. We might have chemical reactions taking place upon the decomposition of a molecule in which a covalence had "degenerated" somewhat, but had not broken down completely to "free" radicals.

The points raised by Prof. Ubbelohde have been most valuable. Clearly solvation, and the formation of complexes from ions such as Fe^{++}, and other electron-transfer agents, must be taken into consideration. As Prof. Evans has pointed out all changes of this type are quantitatively dependent upon the oxidation-reduction potentials of the systems involved, and this is obviously influenced by the exact environments of our reactant ions, molecules and free radicals. To elucidate our reaction-mechanisms more clearly we need to know more about the *difference* in the energy levels of our initial and transition states. In this connection Dr. Birch's survey of reductions is important as it has shown us that in predicting chemical reactivity we must take into consideration not only the structures of our starting materials, but also the resonance states of the alternative possible resultant molecules, ions or transition complexes.

It has interested me to find that a number of contributors to the discussion have commented on possible biological implications of this new field of chemistry. Though we are still far from the stage at which we can give much help to biochemists it is interesting to note that the continuous-flow system which has been described by Dr. Denbigh is very like that of a living cell into which reactants diffuse, and from which products escape. As Dr. Denbigh has told us, these are the conditions under which we can maintain the continuing existence of labile molecules of all types.

Dr. K. G. Denbigh (*Welwyn*) (*communicated*): In reply to Dr. Waters, a paper on the general theory of steady states, and some biological applications, was at present in process of publication by the Society.

IV. POLYMERISATIONS.

INTRODUCTORY PAPER.

By M. G. Evans.

Received 15th September, 1947.

It has now been well established that, in a large number of cases, the polymerisation of ethylenic compounds follows the general scheme:

I. Radical producing reaction C → R. $\quad k_1$

II. $R + \underset{\textstyle X}{CH_2{=}CH} \rightarrow R\,.\,CH_2\,.\,\underset{\textstyle X}{CH}—$ $\quad k_i$

III. $R\,.\,CH_2—\underset{\textstyle X}{CH} + CH_2{=}\underset{\textstyle X}{CH} \rightarrow R\,.\,CH_2\,.\,\underset{\textstyle X}{CH}—CH_2\,.\,\underset{\textstyle X}{CH}—$ $\quad k_p$

IV. $R—\left(CH_2—\underset{\textstyle X}{CH}\right)_n— + —\left(\underset{\textstyle X}{CH}—CH_2\right)_m—R \rightarrow R—\left(CH_2—\underset{\textstyle X}{CH}\right)_{n+m}—R$ $\quad k_t$

Studies of the kinetics of polymerisation reactions are of importance in a survey of free-radical reactions of the radical character of all the above steps. The initiation of polymerisation may be used as evidence of the production of free radicals in step I. The velocity constants of steps II and III would yield information about the reactivity of radicals and of ethylenic double bonds, and investigation of the values of velocity constants of III and IV during the course of polymerisation would tell us whether the reactivity of large radicals was independent of the chain length.

Relative Reactivity of Radicals and Monomers.

Such a reaction scheme as that set out above would lead, on the assumption that k_p and k_t are independent of chain length, to the expression for the rate of polymerisation

$$\frac{dP}{dt} = k_p\sqrt{\frac{k_1 c}{k_t}}\,.\,m$$

and even if an independent determination of k_1 is possible, measurement of the rate of polymerisation yield values of $k_p/\sqrt{k_t}$ and thus by such methods it is only possible to compare under the same conditions, different monomers and obtain relative values of $(k_p/\sqrt{k_t})_a/(k_p/\sqrt{k_t})_b$.

In copolymerisation reactions the growing end of a polymer chain may be a radical of type R_1 arising from monomer M_1 or a radical R_2 arising from monomer M_2. These radicals may each react in two ways, viz.:

$$\begin{cases} \sim\sim R_1 + M_1 \rightarrow \sim\sim R_1 & k_{11} \\ \sim\sim R_1 + M_2 \rightarrow \sim\sim R_2 & k_{12} \end{cases}$$

$$\begin{cases} \sim\sim R_2 + M_1 \rightarrow \sim\sim R_1 & k_{21} \\ \sim\sim R_2 + M_2 \rightarrow \sim\sim R_2 & k_{22} \end{cases}$$

From an investigation [1] of the composition of the copolymers produced under different conditions of M_1 and M_2 the values of k_{11}/k_{12} and k_{21}/k_{22} can be obtained. In other words one can determine the relative reactivity of a radical towards different monomers. A discussion of the results of such studies forms a large part of this section.

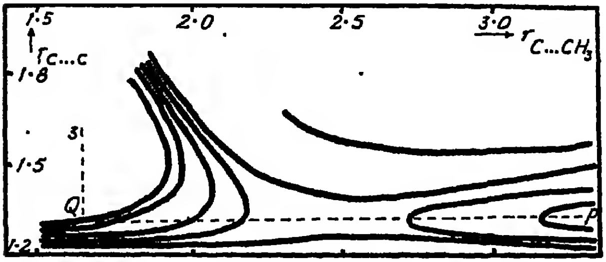


FIG. 1*a*.—Energy contour diagram for reaction.
$CH_3 \ldots CH_2 \rightarrow CH_3—CH_2—CH_2—$
$E = 5{\cdot}1$ kcal.

It is to be noted that in all these reactions the activation energy is small round about 5 kcal. per mole, and hence big changes in velocity constants and in relative reactivities will be brought about by small changes in the activation energy. One has in these measurements, therefore, a very sensitive index of reactivity and of the factors influencing it.

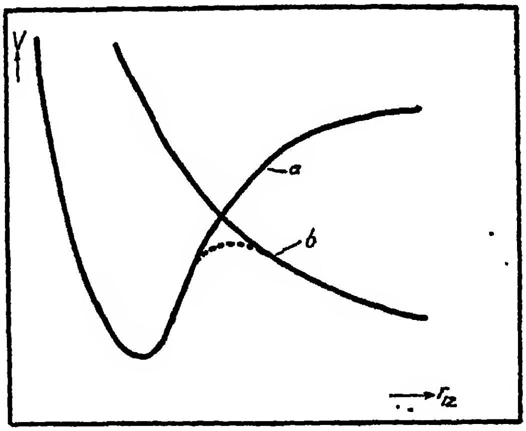


FIG. 1*b*.

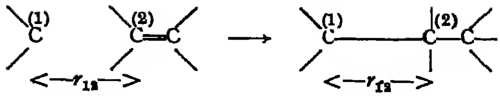
Price and Alfrey [2] have described the reactivity of radicals and monomers in terms of two factors: (1) a factor Q related to the general reactivity of the monomer molecule and the other a factor describing the charge distribution on the attacking radical and the monomer. Thus for the velocity constants k_{11} and k_{12}

$$k_{11}/k_{12} = \frac{Q_1 \exp\{-e_{R_1}e_{M_1}/rDRT\}}{Q_2 \exp\{-e_{R_1}e_{M_2}/rDRT\}} = \frac{Q_1}{Q_2}\exp\{-e_{R_1}(e_{M_1} - e_{M_2})/rDRT\}$$

in which e_{R_1}, e_{M_1} and e_{M_2} are the electronic charges on the reacting centres of the attacking radical and the two monomers respectively. One might associate Q with the resonance energies of the radicals and the monomer molecules. In certain reactions, however, it is clear that factors other than those included in the treatment of Alfrey and Price do come into play. And this seems to be especially true in reactions such as that between styrene and maleic anhydride in which alternating addition occurs.

A method of representing the energy changes accompanying the attack of a radical on a double bond is shown in Fig. 1*b*. Here the potential energy is plotted as a function of co-ordinate r_{12}

[1] Mayo and Lewis, *J. Amer. Chem. Soc.*, 1944, **66**, 1594. Mayo, Lewis and Hulse, *ibid.*, 1945, **67**, 1701. Wall, *ibid.*, 1944, **66**, 2050. Alfrey and Goldfinger, *J. Chem. Physics*, 1944, **12**, 205.
[2] Price and Alfrey, *J. Polymer Sci.*, 1947, **2**, 101. Price, *ibid.*, 1946, **1**, 83.



and is derived from the complete potential energy surface shown in Fig. 1*a** by taking a section along the line PQ.

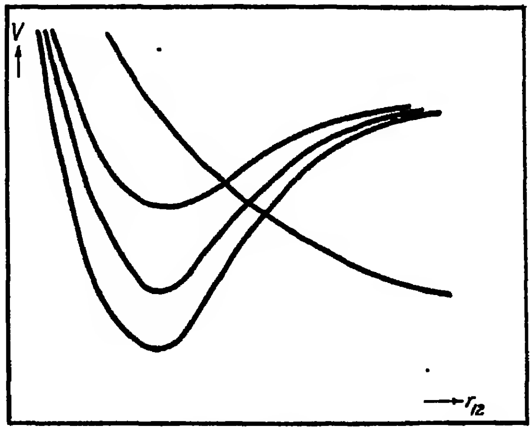


FIG. 1*c*.

Curve *a* represents the repulsion energy between the centres 1 and 2 and Curve *b* the bond extension energy of the single bond in the final state between the centres 1 and 2. The true potential energy curve differs from those representing the bond assignments of initial and the final states by the resonance energy of configurations in the neighbourhood of the crossing point. Fig. 1*c* and 1*d* represent the influences of changes in the heat of reaction and changes in the character of the repulsion curve on the energy of the crossing point, and if we assume that these changes have little influence on the value of the resonance energy at the crossing point, then such changes will influence directly the activation energy.

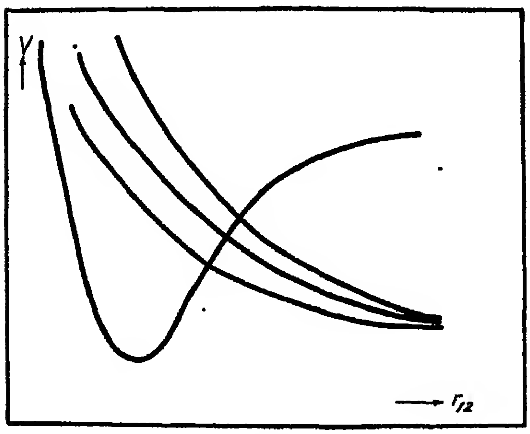


FIG. 1*d*.

In a reaction of the type

$$A + M \rightarrow F$$

in which A is the attacking radical and F the radical formed, the heat of reaction can be split up into the following terms:

$$H = (-R_A - R_M + R_F) - D_{C=C} + D_{C-C}$$

in which R_A is the resonance energy of the attacking radical, R_M that of the monomer molecule and R_F that of the radical formed. Changes in the activation energy accompanying changes in the heat of reaction will on the above assumptions be given by

$$\Delta E = \alpha \Delta H = \alpha(R_A + R_M - R_F)$$

In which α is a factor less than unity.†

* This potential energy surface was calculated by C. E. Seaman using the bond eigen-function method (*Thesis* (Leeds University, 1941)). This work has recently been extended by J. Gergely and the results are shortly to be published.

† For the sodium-flame reaction the value of $\alpha = 0{\cdot}3$ (Polanyi and Warhurst).

We feel this leads to an important principle in the theory of copolymerisation. If, for example, we consider the relative velocities of two copolymerisation steps, both involving the same growing radical, but different monomer molecules,

$$\sim\!\sim\!\sim A_1 + M_1 \rightarrow \sim\!\sim\!\sim F_1$$
$$\sim\!\sim\!\sim A_1 + M_2 \rightarrow \sim\!\sim\!\sim F_2$$

then on the basis of the above argument the ratio of the rate constants, governed by the difference in the activation energy for the two steps, will be

$$\frac{k_{11}}{k_{22}} = \exp\{(-E_{11} + E_{12})/RT\} = \exp - \alpha\{(R_{M_1} - R_{F_1}) - (R_{M_2} - R_{F_2})\}/RT.$$

We would suggest that the term Q defined by Price and Alfrey as a measure of the general reactivity of the monomer is to be understood in these terms.

It is interesting to note that a comparison of the rates of polymerisation of separate monomers does not lead to such important information about the properties of the free radicals involved. Thus a comparison of the velocity constants for the following reactions

$$\sim\!\sim\!\sim A_1 + M_1 \rightarrow F_1(\equiv A_1)$$
$$\sim\!\sim\!\sim A_2 + M_2 \rightarrow F_2(\equiv A_2)$$

leads to

$$k_{11}/k_{22} = \exp - \alpha(R_{M_1} - R_{M_2})/RT,$$

in which only the resonance energy of the monomer molecule is involved.

The second factor influencing the activation energy of polymerisation steps and hence the relative rates in copolymerisation, is the character of the repulsion curve, see Fig. 1*d*. Eyring and Ri [3] have shown how the charge distribution on the centres involved in the reaction may influence the activation energy in the case of the nitration of substituted benzene. and we can apply the same method here to the influence of charge distribution on the attacking radical and the monomer. Changes in the charge distribution on the reacting centres will influence the character of the repulsion curve in Fig. 1*c*. It is unfortunate that our precise knowledge of the magnitudes of these differences in charge distribution is at present very scanty, but at the same time, it is important to note that the results from copolymerisation seem to be in keeping with the general effects of charge distribution which manifest themselves in general organic reactions. In this connection it is interesting to note that the same relationship which Hammett [4] found to apply to the influence of substituents in the benzene ring on the dissociation of constants of acids, the velocity constants for hydrolysis of esters and related reactions, is found by Walling and Mayo to apply to the relative reactivity of substituted styrenes towards the styrene radical. A more precise treatment must await a deeper understanding of the influence of substituents on the electron density of neighbouring centres. A line of approach to this problem which is being further explored is that developed by Pauling and Wheland [5] in their study of the directive effects of substituents in the benzene ring used by Evans and Warhurst [6] in an attempt to understand the influence of substituents on the activation energies of the Diels-Alder reaction.

Another factor influencing the repulsion curve, which cannot be overlooked, in any such treatment of copolymerisation is the steric repulsion between groups not entering directly into the reaction. That this may, in certain cases, become a major factor is very well illustrated by the effect

[3] Eyring and Ri, *J. Chem. Physics*, 1940, 8, 433.
[4] Hammett, *Physical Organic Chemistry* (McGraw Hill Book Co. Inc., New York, 1940).
[5] Pauling and Wheland, *J. Amer. Chem. Soc.*, 1935, **57**, 2091.
[6] Evans and Warhurst, *Trans. Faraday Soc.*, 1938, **34**, 614.

of substituents X and Y in compounds of the type $CH_2{=}C\langle^X_Y$ on the heat of polymerisation, as for example in the case of *iso*butyene,[7] methyl methacrylate and other methacrylic esters.[8]

In the above qualitative treatment it has been assumed, in order to isolate the influences of the heat of reaction and the character of the repulsion curve, that changes in the resonance energy in the transition state accompanying changes in the radicals and monomers, are small, and that the major changes are those affecting the energy of the crossing point. This will not always be the case and in some reactions the changes in resonance energy in the transition state accompanying changes in structure may well be the determining factor. The importance of a high resonance energy in the transition state has been emphasised in a discussion on the low activation energies of Diels-Alder[9] reactions, and the influence of negative groups on the rate of sodium-flame reactions[10] has been explained by the additional resonance energy arising from an increase in the possible number of electron assignments in the transition state. Walling and Mayo introduce a very similar idea in their discussion of alternating polymerisation.

The Absolute Velocity Constants of Radical Polymerisation Steps.

We have pointed out that the kinetic treatment of polymerisation in the cases of radical initiation does not afford a method of determining the absolute values of the velocity constants k_p and k_t, nor does it enable one to decide whether these constants are dependent or not on the length of the growing- or termination-polymer chains. In the case of photo-initiated polymerisation, however, Melville[11] and Bartlett[12] have shown that by using the rotating sector method it is possible to measure the life-time of the growing chains and to determine the individual values of k_p and k_t. For the case of liquid vinyl acetate Melville obtained the following results :

k_p (l. mol.$^{-1}$ sec.$^{-1}$)	$7{\cdot}7 \times 10^2$	$6{\cdot}7 \times 10^2$	$E_p = 4{\cdot}4$ kcal./mole $A_p = 1{\cdot}65 \times 10^6$ l.g. mol.$^{-1}$ sec.$^{-1}$.
k_t (l. mol.$^{-1}$ sec.$^{-1}$	$3{\cdot}1 \times 10^9$	$2{\cdot}5 \times 10^9$	$E_t = 0$
Chain length	174	339	

These results show the following features.

1. The activation energy for the addition of a monomer molecule to a growing radical chain is about 5 kcal. per mole. This activation energy is similar to that obtained for radical and atom reactions in the gas phase and is in keeping with the theoretical picture of such reactions.

2. The chain-termination reaction apparently requires no activation, a result which may well point to the conclusion that the termination step involves the dimerisation of two radicals rather than a dismutation, for

[7] Evans and Polanyi, *Nature*, 1943, 152, 738.
[8] Baxendale, Evans, McLeavy and Fearnley (unpublished results).
[9] Evans, *Trans. Faraday Soc.*, 1939, 35, 824. Evans and Warhurst, *ibid.*, 1938, 34, 614.
[10] Evans and Polanyi, *Nature*, 1941, 148, 436.
[11] Burnett and Melville, *ibid.*, 1945, 156, 661 ; *Proc. Roy. Soc. A*, 1947, 189, 456.
[12] Bartlett and Swain, *J. Amer. Chem. Soc.*, 1945, 67, 2273. Nozaki and Bartlett, *ibid.*, 1946, 68, 2377.

one might expect the dismutation reaction, which involves the transfer of a hydrogen atom, to have a small activation energy. Melville, however, concludes from the kinetics, that termination is not radical dimerisation.

We should only expect a radical-dimerisation termination to occur with no activation energy and a temperature-independent factor independent of chain length under conditions where the diffusion of the growing polymer chains is not a rate-determining step. Under conditions of high viscosity it may well happen that this process does become rate determining when the termination process would show an activation energy related to that for viscous flow and the temperature-independent factor would become dependent upon chain length in the same way as does viscosity.

3. The velocity constants of both propagation and termination appear to be independent of chain lengths. If this effect is found to be common to such reactions, a great simplification can be introduced into the kinetic treatment.

4. The temperature-independent factor for chain growth is much smaller than that for chain termination. It might be possible to understand the relatively small temperature-independent factor for chain growth in terms of the restriction in the motion of the monomer molecule when it passes from the free state to that of a unit in the polymer chain.

Bamford and Dewar have used this same method in a study of the photo-initiated polymerisation of styrene and methyl methacrylate. They employ, for the analysis of their results, a more complicated kinetic scheme. They do find, however, the same general features, namely, a low temperature-independent factor for the chain propagation step and activation energy of the order of 6 kcal. per mole. A new feature in the case of styrene, which they attribute to the low reactivity of the styrene radicals, is the small activation energy of 3 kcal. for the termination reaction.

Chain-transfer and Chain-termination Reactions.

Chain-transfer reactions occur by steps of the type

$$\sim\sim CH_2— + XS \rightarrow \sim\sim CH_2X + S— \quad k_{SX}$$

$$S— + CH_2{=}CH_2 \rightarrow S—CH_2—CH_2— \quad k_{ri}$$

We thus see that two separate processes are involved, one the transfer of the centre X to the growing free radical and secondly, the reinitiation of polymerisation by the new radical S produced in the first step. If all the new radicals S are used in restarting chains then Mayo [13] has shown that a simple relationship exists between the degree of polymerisation P and the chain-transfer coefficient C

$$\frac{1}{P} = \frac{C[SX]}{[M]} + \frac{1}{P_0}$$

in which C is the ratio of the velocity constant for the reaction

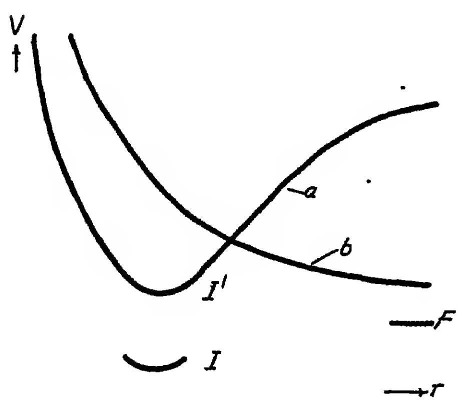


FIG. 2a.

$$\sim CH_2— + XS \rightarrow \sim\sim CH_2X + S— \quad k_{SX}$$

[13] Mayo, *J. Amer. Chem. Soc.*, 1943, 65, 2324.

and that for the reaction

$$\sim\sim CH_2— + M \rightarrow \sim\sim CH_2— \qquad k_p$$

and P_0 is the degree of polymerisation in the absence of the chain-transfer agent.

The chain-transfer coefficient is thus a comparison of the reactivity of the growing polymer chain for reaction with the compound SX with that of the chain growth step. By using a variety of chain-transfer agents SX in the same polymerising system, it is thus possible to compare the relative rates of step k_{SX} above.

In terms of potential energy curves we can represent the reaction

$$\underset{<\cdots r \cdots>}{—R— \quad X}—S \rightarrow —\underset{<\cdot r \cdot>}{R——X}\,.—S$$

in terms of the co-ordinate r. This is shown in Fig. 2*a*. Point I represents the energy of the initial bond assignment, I′ the energy of the system when the radical R has approached to within the critical reaction distance of the centre X. Curve *a* shows the energy of extension of the SX bond and curve *b* the repulsion energy between the centre S and the molecule RX. Point F denotes the energy of the system in its final state. We can express in terms of this diagram the influence which changes in S will have on the activation energy of the transfer process, and it is seen in Fig. 2*b* that changes in S which decrease the bond strength will decrease the activation energy of the transfer process. In this connection it is interesting to enumerate the changes which workers have found to increase the efficiency of chain transfer. Mayo has shown that increasing substitution on a carbon centre increases the reactivity of the hydrogens on that centre for reaction in the chain-transfer process. This is shown by a comparison of toluene, ethyl benzene and *iso*propyl benzene. This sequence is in keeping with the changes in bond strength of carbon halogen bonds found by Polanyi [14] and his co-workers in the series methyl, ethyl, *iso*propyl, *tert*butyl. And the comparison of toluene, diphenyl methane, triphenyl methane and pentaphenyl ethane also form an interesting series, in which it is clear that the increasing resonance energy of the radical S leading to a decrease in the energy of dissociation of the compound SX brings about a greatly increased efficiency in chain transfer (see Table I).

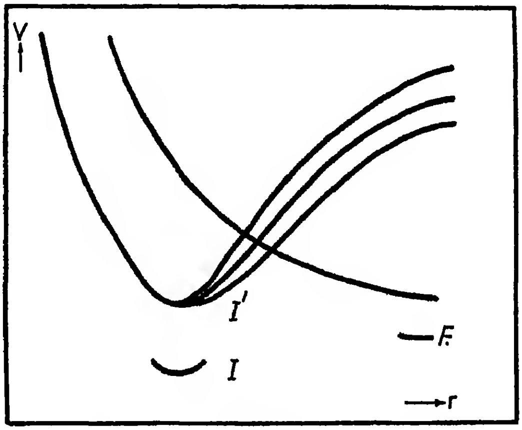


FIG. 2*b*.

The work reported by Melville and Burnett, and by Bamford and Dewar, shows that the efficiency of halogen containing compounds in reaction k_{SX} above, follows a sequence which in other reactions has likewise been attributed to a decrease in the bond strength (see Table II).

One would expect, however, that changes in the character of S which lead to big decreases in the bond strength SX by stabilisation of the radical S would, while increasing the efficiency of reaction k_{SX}, decrease the rate of

[14] Baughan and Polanyi, *Nature*, 1940, 146, 685.

the reinitiation reaction k_{r_1}. Thus, while we might expect the activation energy of the first step to be given by

$$E = (E_0 - \alpha_1 R_S)$$

that of the second step would be given by

$$E = (E_0 + \alpha_2 R_S)$$

TABLE I.

Compound	$C_6H_5CH_2$—H	$(CH_3)(C_6H_5)$CH—H	$(CH_3)_2(C_6H_5)$C—H
C. Chain transfer coefficient × 10^5	1·25	6·7	8·2
Compound	CH_3CH_2—H	$(CH_3)_2$CH—H	$(CH_3)_3$C—H
Bond strength * D_{C-H} kcal /mole .	96·4	91·0	86·9

Compound	$C_6H_5CH_2$—H	$(C_6H_5)_2$CH—H	$(C_6H_5)_3$C—H
C. Chain transfer coefficient × 10^5 . . .	1·25	23	35
Radical resonance energy (calculated) † . .	0·72 β ‡	1·30 β	1·80 β

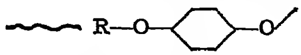
TABLE II.

Compound . . .	Cl.C_2H_4.Cl	$CHCl_3$	CCl_4	$C_2H_4Br_2$	CBr_4
k_{SX} (vinyl acetate) at 54·0° c.	—	207	430	—	—
k_{SX} (styrene) at 60° c. .	1·9 × 10^{-3}	—	0·804	3·25 × 10^{-2}	159
Collision efficiency in Na-flame reaction § . .	1·25 × 10^{-3}	0·01	0·04	1·33 × 10^{-2}	—

Hence, if the radical S formed is sufficiently stable, the process will become one of chain termination. Indeed this may be the mechanism of chain termination with hydroquinones. Bolland and ten Have have shown that hydroquinones are efficient chain terminators for an oxidation

* Baughan and Polanyi, *Nature*, 1940, **146**, 685.
† Wheland, *Ann. N.Y. Acad. Sci.*, 1940, **40**, 77.
‡ β = the resonance integral.
§ Cremer, Curry and Polanyi, *Z. physik. Chem.*, *B*, 1933, **23**, 445.

chain, because of the inability of the semiquinone radical so formed to initiate a further radical reaction, and the work of Bartlett suggests that quinones inhibit by the formation of a semiquinone of the type :



It would seem that the main features of radical reactions in polymerisation can, in certain cases, be understood in terms of bond energies and the resonance energies of radicals, and that our knowledge of the relative reactivity of both radicals and monomers has advanced very rapidly through the studies of copolymerisation. There are, however, many details to be filled in, notably the influence of substituents on the charge distribution in both radicals and monomers, and an understanding of this in terms of quantum-mechanical treatments is perhaps one of the most important theoretical studies of the next few years. Important though these relative values are in our understanding of chemical reactivity, it will be necessary for any complete quantitative treatment, to obtain as much information as possible about the absolute values of the velocity constants involved, and by an evaluation of the activation energies to investigate how radical structure and size affect the energetics and the entropy changes in radical reactions.

A.—REACTIONS OF RADICALS AND MONOMERS.

(*a*) INITIATION.

N-NITROSOACYLARYLAMINES AS CATALYSTS IN ADDITION POLYMERISATION.

By D. H. Hey and G. S. Misra.

Received 15th August, 1947.

In 1934 [1,2] it was shown that four different types of compound, represented by benzenediazo hydroxide, nitrosoacetanilide, phenylazotriphenylmethane and benzoyl peroxide, displayed certain characteristic features in reactions with aromatic compounds which clearly differentiated such reactions from normal electrophilic and nucleophilic substitution processes. A homolytic reaction mechanism was therefore put forward to explain these apparently abnormal reactions which involved the formation of unstable reactive free radicals as intermediates. The general acceptance of these views implied that benzenediazo hydroxide, nitrosoacetanilide and phenylazotriphenylmethane should act in the same manner as benzoyl peroxide in initiating the polymerisation of vinyl compounds and it was not long before examples of each type were tested for catalytic activity. Price and Durham [3] were able to show that benzenediazo hydroxides were able to catalyse the polymerisation of styrene, while somewhat earlier the effectiveness of phenylazotriphenylmethane had been clearly demonstrated by Schulz.[4] The use of *N*-nitrosoacylarylamines as catalysts in addition polymerisation was convincingly demonstrated by Blomquist, Johnson and Sykes.[5]

The generally accepted theory of addition polymerisation implies that the primary active agent is a free radical and that such free radicals

[1] Hey and Grieve, *J. Chem. Soc.*, 1934, 1797. [2] Hey, *ibid.*, 1934, 1966.
[3] Price and Durham, *J. Amer. Chem. Soc.*, 1942, 64, 2508.
[4] Schulz, *Naturwiss.*, 1939, 27, 659.
[5] Blomquist, Johnson and Sykes, *J. Amer. Chem. Soc.*, 1943, 65, 2446.

become incorporated in the polymer molecules as end-groups. This has been demonstrated by using free radicals containing atoms or groups which lend themselves to qualitative detection and, in many cases, to quantitative estimation. When *p*-bromobenzoyl peroxide, for example, was used in place of benzoyl peroxide as catalyst for the polymerisation of styrene the polymer thus formed contained both *p*-bromophenyl and *p*-bromobenzoyloxy groups.[6] These groups obviously result from the initial decomposition of the *p*-bromobenzoyl peroxide into the two different free radicals, thus :

$$p\text{-Br}.C_6H_4CO.O.O.CO.C_6H_4.\text{Br-}p \rightarrow p\text{-Br}.C_6H_4^{\bullet} + p\text{-Br}.C_6H_4.CO.O^{\bullet} + CO_2$$

When *N*-nitrosoacylarylamines were used as catalysts Blomquist, Johnson and Sykes (loc. cit.) were able to show that fragments of the catalyst molecules were found in the polymers formed from styrene, methyl methacrylate and acrylonitrile but they claimed that only the active free aryl radicals produced in the decomposition of the *N*-nitrosoacylarylamines were so incorporated in the polymer molecules and the free acyloxy radicals did not appear to be involved. The *N*-nitrosoacylarylamines used in these reactions were mainly *N*-nitroso-*p*-bromoacetanilide, *NN'*-dinitroso-4 : 4'-dibromosuccindianilide, *N*-nitroso-α-bromo*iso*valeranilide and *N*-nitroso-*N*-phenyl-*m*-bromobenzamide. In those cases in which bromine is attached directly to the aromatic group, bromine was found in the polymer in quantities varying between 0·80 and 7·50 %, whereas in the cases in which bromine is attached to the acyloxy group no bromine was found as shown by a negative Beilstein test and a negative test after fusion with sodium. There would seem to be no clear reason why both aryl and acyloxy radicals should become incorporated in the polymer when peroxides are used whereas only the aryl radicals are involved with the nitrosoacylarylamines as catalysts. The initial decomposition of both types of compound is very similar in character as may be seen in the following equations :

$$R.CO.O.O.CO.R \rightarrow R.CO.O. + R^{\bullet} + CO_2$$

$$\begin{array}{l} R.N(NO).COR \\ \quad\ \downarrow\uparrow \\ R.N{=}N.O.COR \longrightarrow R.CO.O. + R^{\bullet} + N_2 \end{array}$$

An examination of the experimental evidence cited by Blomquist, Johnson and Sykes shows that their conclusion, that only the active free aryl radicals produced in the decomposition of the nitrosoacylarylamines are incorporated in the polymer molecules, rests solely on negative qualitative tests for bromine using the Beilstein test and fusion with sodium. Since the bromine content would in any case be very small it seemed desirable that this aspect of the subject should be given further study and some polymerisation reactions have now been carried out on styrene, methyl methacrylate and acrylonitrile using in turn *N*-nitroso-*p*-bromoacetanilide, *N*-nitroso-*N*-phenyl-*m*-bromobenzamide and *N*-nitroso-*N*-phenyl-*p*-bromobenzamide as catalysts. The polymers formed in these reactions were carefully purified and analysed for bromine.

Using *N*-nitroso-*p*-bromoacetanilide as catalyst polymerisation reactions were carried out with styrene, methyl methacrylate and acrylonitrile and the carefully purified polymers were found to contain from 1·61 to 8·64 % bromine, thus confirming the incorporation of *p*-bromophenyl groups in the polymer molecules. When *N*-nitroso-*N*-phenyl-*m*-bromobenzamide was used with both styrene and methyl methacrylate the presence of bromine was again detected in the purified polymer and similar results were obtained when *N*-nitroso-*N*-phenyl-*p*-bromobenzamide

[6] Bartlett and Cohen, *J. Amer. Chem. Soc.*, 1943, 65, 543.

was used as a catalyst. These results indicate that, contrary to the conclusions of Blomquist, Johnson and Sykes, when *N*-nitrosoacylarylamines are used as catalysts both the phenyl and the acyloxy groups are incorporated in the polymer molecules.

Experimental.

Materials :

STYRENE, METHYL METHACRYLATE, ACRYLONITRILE.—These materials were distilled immediately before use.

N-NITROSO-*p*-BROMOACETANILIDE. This compound was prepared in 90 % yield from *p*-bromoacetanilide and nitrosyl chloride using the method of France, Heilbron and Hey.[7] It melted at 84-86° with explosive decomposition. Hantzsch and Wechsler [8] recorded m.p. 88°.

N-NITROSO-*N*-PHENYL-*m*-BROMOBENZAMIDE. *N*-Phenyl-*m*-bromobenzamide was prepared from aniline and freshly distilled *m*-bromobenzoyl bromide. After crystallisation from absolute alcohol it melted at 145-147°, whereas Kottenhahn [9] recorded m.p. 137° (Found : C, 56·3 ; H, 3·8. $C_{13}H_{10}ONBr$ requires C, 56·5 , H, 3·65 %). The nitroso compound, prepared in almost quantitative yield by the method of France, Heilbron and Hey, decomposed at 68·5°, whereas Blomquist, Johnson and Sykes recorded m.p. 61° for their catalyst.

N-NITROSO-*N*-PHENYL-*p*-BROMOBENZAMIDE. *N*-Phenyl-*p*-bromobenzamide, prepared from aniline and *p*-bromobenzoyl chloride, crystallised from alcohol in prisms, m.p. 202-204°. The nitroso compound was prepared in almost quantitative yield using nitrosyl chloride as in the preceding examples. It melted at 73° with explosive decomposition.

Polymerisation.—All reactions were carried out with freshly prepared catalysts. The molecular weights of the various polymers were determined from viscosity measurements in benzene solution. For the samples of polystyrene the revised equation of Kemp and Peters,[10] viz.

$$M = \frac{K_{em} . \log \eta_r}{C}$$

where η_r is the specific viscosity, C is the fundamental molarity, and $K_{em} = 0·45 \times 10^4$, was used. For the polymers prepared from methyl methacrylate the original Staudinger equation, $M = \eta_{sp}/C . K_m$ where $K_m = 1·7 \times 10^{-4}$, was used. Molecular weight measurements were not carried out in the case of the polyacrylonitriles owing to their insolubility.

Polymerisation of Styrene.—(i) A mixture of styrene (20·24 g.) and *N*-nitroso-*p*-bromoacetanilide (1·24 g.) was maintained at 75° for 24 hr. The crude polymer (15 g.) was isolated by dissolving the reaction mixture in dioxane and adding methyl alcohol. The purified polymer (3·56 g.) was obtained after three such precipitations (Found : C, 90·07 ; H, 7·72 ; Br, 2·94 %. Mol. Wt., 5940. Br. $C_6H_4 . (C_8H_8)_{54} . C_6H_5$. Br requires C, 89·89 ; H, 7·47 ; Br, 2·70 % Mol. Wt., 5931).

(ii) A mixture of styrene (9·074 g.) and *N*-nitroso-*N*-phenyl-*m*-bromobenzamide (0·464 g.) was heated in a sealed ampoule at 100° for 24 hr. The resulting polymer (4 g.) was dissolved in dioxane and precipitated by pouring into an excess of methyl alcohol. The purified polymer was obtained after three precipitations (Found : C, 90·84 ; H, 7·52 %; Br, traces. Mol. Wt., 13,760).

Polymerisation of Methyl Methacrylate.—(i) *N*-Nitroso-*p*-bromoacetanilide (4·87 g.) was added to methyl methacrylate (28·02 g.) at room temperature. After about ½ hr. the mixture became warm and darkened in colour. The reaction flask was surrounded by cold water and left for 16 hr. The entire mixture, which solidified, was dissolved in dioxane and precipitated with methyl alcohol and this process was repeated several times to give the pure polymer (2·5 g.) (Found : C, 54·64 ; H, 7·47 ; Br, 1·61 %. Mol. Wt., 11,060).

(ii) A mixture of *N*-nitroso-*N*-phenyl-*m*-bromobenzamide (1·529 g.) and methyl methacrylate (10 cc.) was left in a sealed ampoule maintained at 20° for 18 hr. When the tube was opened a considerable pressure had developed

[7] France, Heilbron and Hey, *J. Chem. Soc.*, 1940, 369.
[8] Hantzsch and Wechsler, *Annalen.*, 1902, **325**, 242.
[9] Kottenhahn, *ibid.*, 1891, **264**, 174.
[10] Kemp and Peters, *Ind. Eng. Chem.*, 1942, **34**, 1097.

due to N_2 evolution. The reaction product was dissolved in dioxane and precipitated with methyl alcohol. The crude polymer (7 g.) was further purified by three precipitations (Found: C, 59·28; H, 7·94; Br, 0·65. Mol. Wt., 18,990. $Br.C_6H_4.CO_2(C_5H_8O_2)_{186}C_6H_5$ requires C, 59·95; H, 7·93; Br, 0·42 %. Mol. Wt., 18,877).

(iii) A mixture of *N*-nitroso-*N*-phenyl-*m*-bromobenzamide (1·50 g.) and methyl methacrylate (10 cc.) was heated in a sealed tube at 79° for 18 hr. The crude polymer (3 g.) was isolated and purified as described above (Found: C, 59·82; H, 8·27; Br, 0·06; Mol. Wt., 19,430. $Br.C_6H_4CO_2(C_5H_8O_2)_{190}C_6H_5$ requires C, 59·94; H, 7·98; Br, 0·41 %. Mol. Wt., 19,300).

Catalyst.	Concn. of Catalyst. Mol./l.	Monomer.	Concn. of Monomer. Mol./l.	Temp.	Time (Hr.).	% Br.	Mol. Wt.	Approx. No. of Fragments, Polymer Molecule.
N-nitroso-*p*-bromo-acetanilide	0·23	Styrene	8·72	75°	24	2·94	5,940	2·18
N-nitroso-*p*-bromo-acetanilide	0·76	Methyl Meth-acrylate	10·00	18°	16	1·61	11,060	—
N-nitroso-*p*-bromo-acetanilide	0·40	Acrylo-nitrile	15·00	19-20°	44	8·64	—	—
N-nitroso-*p*-bromo-acetanilide	0·10	Acrylo-nitrile	3·64	60°	2	6·94	—	—
N-nitroso-*N*-phenyl-*m*-bromo-benzamide	0·152	Styrene	8·72	100°	24	Traces	13,760	—
N-nitroso-*N*-phenyl-*m*-bromo-benzamide	0·501	Methyl Meth-acrylate	10·00	20°	18	0·65	18,990	2·54
N-nitroso-*N*-phenyl-*m*-bromo-benzamide	0·493	Methyl Meth-acrylate	10·00	79°	18	0·06	19,430	1·14
N-nitroso-*N*-phenyl-*p*-bromo-benzamide	0·656	Methyl Meth-acrylate	10·00	20°	16	0·32	55,240	2·20 3·13
N-nitroso-*N* phenyl-*p*-bromo-benzamide	0·656	Methyl Meth-acrylate	10·00	79°	16	0·26	17,110	1·56
N-nitroso-*N*-phenyl-*p*-bromo-benzamide	0·218	Methyl Meth-acrylate	3·15	68·7°	5	0·34	8,900	1·38

(iv) A mixture of *N*-nitroso-*N*-phenyl-*p*-bromobenzamide (2 g.) and methyl methacrylate (10 cc.) was maintained at 20° for 16 hr. The crude polymer (5 g.) was isolated and purified as described above (Found: C, 59·19; H, 8·55; Br, 0·32. Mol. Wt., 55,240. $Br.C_6H_4CO_2(C_5H_8O_2)_{548}CO_2C_6H_4.Br$ requires C, 59·82; H, 8.00; Br, 0·29. Mol. Wt., 55,285. $Br.C_6H_4CO_2(C_5H_8O_2)_{548}.C_6H_5$ requires C, 59·98; H, 8·04; Br, 0·15 %. Mol. Wt., 55,077).

(v) A mixture of *N*-nitroso-*N*-phenyl-*p*-bromobenzamide (2·00 g.) and methyl methacrylate (10 cc.) was maintained in a sealed tube at 79° for 16 hr. The crude polymer (5 g.) was isolated and purified as described above (Found: C, 59·34; H, 8·22; Br, 0·26; Mol. Wt., 17,110. $Br.C_6H_4CO_2(C_5H_8O_2)_{170}.C_6H_5$ requires C, 59·69; H, 8·02; Br, 0·46 %. Mol. Wt., 17,208).

(vi) A mixture of N-nitroso-N-phenyl-p-bromobenzamide (2 g.), methyl methacrylate (10 cc.) and n-hexane (20 cc.) was boiled under reflux for 5 hr. After evaporation of the n-hexane, the residue was dissolved in dioxane and poured into excess of methyl alcohol. Addition of a little water precipitated the polymer (1 g.), which was purified by thrice dissolving in dioxane and pouring into an excess of ice-cold methyl alcohol (Found: C, 59·48; H, 7·96; Br, 0·34; Mol. Wt., 8900. $Br . C_6H_4 . CO_2 . (C_5H_8O_2)_{88} . C_6H_5$ requires C, 59·77; H, 7·90; Br, 0·90 %; Mol. Wt., 8900).

Polymerisation of Acrylonitrile.—(i) A mixture of N-nitroso-p-bromoacetanilide (1·77 g.) and acrylonitrile (16·04 g.) was maintained at 19-20° for 44 hr. The crude polymer was collected by filtration and impurities were removed by continuous extraction with ether and methyl alcohol successively. The purified polymer weighed 1·5 g. (Found: C, 61·63; H, 5·19; N, 22·60; Br, 8·64 %).

(ii) A mixture of N-nitroso-p-bromoacetanilide (1·48 g.), acrylonitrile (12·78 g.) and benzene (50 cc.) was maintained at 60° for 2 hr. The crude polymer was collected by filtration and purified as described above (Found: C, 63·72; H, 5·24; N, 21·90; Br, 6·94 %).

Summary of Results.

The foregoing results are summarised in the preceding table which shows the approximate number of catalyst fragments contained in the polymers.

Summary.

It has been shown that N-nitrosoacylarylamines will effect the polymerisation of styrene, methyl methacrylate and acrylonitrile and that the resulting polymers contain both the aryl and acyloxy groups which result from the decomposition of the catalyst.

Résumé.

On a montré que les N-nitrosoacylarylamines affectent la polymérisation du styrène, du méthacrylate de méthyle et de l'acrylonitrile et que les polymères résultants contiennent à la fois les groupes aryl et acyloxyl, qui proviennent de la décomposition du catalyseur.

Zusammenfassung.

Es ist gezeigt worden, dass N-Nitrosoacylarylamine die Polymerisation von Styrol, Methylmethacrylat und Acrylonitril bewirken und die gebildeten Polymeren sowohl die Aryl- als auch die Acyloxygruppen enthalten, die die Folge der Zersetzung des Katalysators sind.

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GENERAL DISCUSSION.

Dr. G. Salomon (*Delft*) said: Although Hey and Misra have demonstrated that no principle difference between the radicals $C_6H_5^{\bullet}$ and $C_6H_5 . COO^{\bullet}$ exists, I am not convinced that the findings of Blomquist *et al* have to be discarded altogether. It may easily be that both radicals differ sufficiently in reactivity to find, under suitable conditions, differences in their ability to initiate chains.

We have found that diazo-aminobenzene, a source of $C_6H_5^{\bullet}$ radical, is a much more powerful initiator for the homogeneous polymerisation of dienes than benzoyl peroxide a source of C_6H_5 $COO^{\bullet}$ and C_6H_5 radicals.

Prof. D. H. Hey (London) said: There appears to be little difference between the reactivity of aryl and aromatic acyloxy radicals since, when p-bromobenzoyl peroxide was used as a catalyst in the polymerisation of

styrene, it had been shown by Bartlett and Cohen that 64 % of the bromine in the polymer molecule was present as *p*-bromobenzoyloxy and 36 % as *p*-bromophenyl. In the experiments referred to by Dr. Baxendale an aliphatic acyloxy group was involved and in this case there may be a greater differentiation between the properties of the two radicals present in the system. Blomquist, Johnson and Sykes had used nitrosoacylarylamines which contained aromatic and aliphatic acyl groups. In our experiments we confined our observations to experiments with aromatic acyloxy groups in order to simulate more closely the conditions which exist when benzoyl peroxides are used. The bromine content of the polymers is admittedly low and attempts are now being made to modify the experimental conditions in order to obtain polymers of shorter chain-length and consequently higher bromine content.

Prof. A. V. Tobolsky (*Princeton*) said: The question raised by Prof. Hey as to the possibilities of *both* radical fragments from various catalysts such as benzoyl peroxide and *N*-nitrosoacylarylamines being effective in initiating addition polymerisation is of outstanding importance with respect to the question of diradical initiation. Recent experiments by H. A. Shah, F. Leonard and A. V. Tobolsky presented at the September 1947 meeting of the A.C.S. in New York, indicate that the degree of polymerisation during phthaloyl polyperoxide-catalysed polymerisation of styrene continues to increase with increasing conversion. The interesting possibility exists that by the use of diradical-producing catalysts, such as ring or polymeric chain peroxides, one may perhaps obtain rapid polymerisation without sacrificing chain length.

Dr. M. Magat (*Paris*) (*partly communicated*): There exists a temperature-independent method other than the photochemical one to produce a known amount of free radicals. This is the Szillard effect. If certain compounds, e.g. ethyl bromide, are irradiated by slow neutrons, these are captured by bromine with subsequent emission of γ-rays. The recoil of the photon is sufficient to break the C—Br link and to produce a Br atom and a $C_2H_5\cdot$ radical. It is very probable that at least one of them, if not both, will start a polymerisation chain. The amount of free radicals formed can be easily evaluated, since the Br atoms set free are radioactive. Some preliminary experiments carried out by Joliot have shown that polymerisation can be initiated by neutrons, but no quantitative measurements have yet been made. We intend to start some research along this line in the near future, but we think the field is a very broad one, and we would be only too happy if other colleagues would collaborate.

One has naturally to bear in mind that the radioactive bromine emits β-rays which in turn may be capable of producing new free radicals. But we think that this effect can be also quantitatively accounted for.

Also, it may be possible to create free radicals by bombarding hydrocarbons with fast neutrons, which cause rupturing of the C—H bond. We are not yet quite sure that this method can be worked out into a quantitative one.

Prof. M. G. Evans and Mr. J. H. Baxendale (*Leeds*) (*communicated*): In connection with the observations reported by Hey and Misra we would like to refer to work done by Mr. L. G. Wood.[1]

Wood studied the polymerisation of methylmethacrylate and of styrene initiated by the decomposition products of *N*-nitrosoacetanilide. The radicals produced in the primary reaction step of the decomposition are presumably phenyl and acetoxy. If this system behaves in the way indicated by the work of Blomquist, Johnson and Sykes we should not expect the acetoxy group to be incorporated in the polymer. The probable fate of this radical, which appears not to attack the double-bond, is to form acetic acid by an oxidative attack on either the solvent or the mono-

[1] Wood, *Thesis* (Leeds University, 1947), "Kinetics of decomposition of *N*-nitrosoacetanilide and the reactions of the free radicals produced".

mer. The determination of acetic acid formed from N-nitrosoacetanilide in the presence and absence of a polymerisable monomer indicates that there is no difference in the amounts produced under these two sets of conditions.

It would seem, therefore, from the results of Misra and Hey that there is a fundamental difference in behaviour between the aromatic and the aliphatic acid radicals in that the latter appear to be oxidative in their action and do not attack and open a double-bond.

(b) PROPAGATION.

COPOLYMERISATION: THE EFFECTS OF STRUCTURE ON THE REACTIONS OF ETHYLENIC BONDS WITH FREE RADICALS.

By Frank R. Mayo, Frederick M. Lewis and Cheves Walling.

Received 6th August, 1947.

The object of this paper is to consider the contribution of researches on copolymerisation to our knowledge of the behaviour of free radicals in solution, using chiefly data which have been published from this laboratory [1a-c] or which will soon appear [1d-l]. The whole development is based on the assumption that the relative rates at which two monomers, M_1 and M_2, enter a copolymer depend only on the reactivities of the two monomers with the terminal groups on the two kinds of free radicals present, the length and composition of the radicals beyond the terminal group being neglected. Neglecting chain initiation and termination, there are then only four reactions which contribute to the composition of the copolymer:

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot \quad (1)$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot \quad (2)$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot \quad (3)$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot \quad (4)$$

The composition of the copolymer is given by [2]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad (5)$$

and depends on the composition of the feed and on the two monomer reactivity ratios, $r_1(= k_{11}/k_{12})$ and $r_2(= k_{22}/k_{21})$. A monomer reactivity ratio greater than one indicates a tendency of the radical to perpetuate its own kind while a ratio less than one indicates a preference for reaction with the other monomer. By a series of copolymerisations of a reference monomer with other monomers, the relative reactivities of the other monomers toward the reference radical can be determined. The monomer reactivity ratios for any chosen pair of monomers are determined by the use of eqn. (5), or its integrated form,[1a] at least two different experiments

[1] (a) Mayo and Lewis, *J. Amer. Chem. Soc.*, 1944, **66**, 1594; (b) Lewis, Mayo and Hulse, *ibid.*, 1945, **67**, 1701; (c) Walling and Briggs, *ibid.*, 1945, **67**, 1774. *J. Amer. Chem. Soc.* (in press): (d) Lewis, Walling, Cummings, Briggs and Mayo, (e) Mayo, Walling, Lewis and Hulse, (f) Doak, (g) Lewis, Walling, Cummings, Briggs, and Wenisch, (h) Mayo, Lewis and Walling, (i) Lewis and Mayo, (j) Walling, Briggs, Wolfstirn and Mayo, (k) Walling, Cummings and Briggs, (l) Mayo, Van Meter and Alderman.

[2] Alfrey, Mayo and Wall, *J. Polymer Sci.*, 1946, **1**, 581.

TABLE I.—MONOMER REACTIVITY RATIOS IN PEROXIDE-CATALYSED COPOLYMERISATIONS AT 60°.

No.	Reference Radical ($M_1\cdot$). Monomer (M_2).	Monomer Reactivity Ratios (r_1) in Copolymerisation of M_1 and M_2 (M_1 corresponding to key number at left).†									
		(2)	(3)	(6)	(7)	(8)	(9)	(12)	(13)	(17)	(19)
1.	Butadiene	0·78*[e]	0·25[c]								
2.	Styrene	(1·00)*	0·46*	0·04°	0·10*	0·18*	0·14°	0·02°	0·01	0·01°	0·07*
3.	Methyl methacrylate	0·52*	(1·00)*	0·18°			0·24		0·015°	0·01°	
4.	Methyl vinyl ketone	0·29[b]		0·61*[e]							
5.	Methacrylonitrile	0·3[bb]	0·67*[d]								
6.	Acrylonitrile	0·40	1·35*	(1·00)*			0·37	0·02°	0·061		
7.	β-Chloroethyl acrylate	0·54*			(1·00)*	0·8*				0·01°	
8.	Methyl acrylate	0·75*			0·8*	(1·00)*	1°		0·1°		
9.	Vinylidene chloride	1·85*	2·53*	0·91*		1°	(1·00)*	0·3°	0·01°		0·046°
10.	Methallyl chloride	22°	7·5°				1·1°	0·3[c,m]	0·13°[i]		
11.	Methallyl acetate	71	10°		4		2·4°				
12.	Vinyl chloride	17	13°	3·28*		5°	3°	(1·00)*	0·23*		0·47
13.	Vinyl acetate	55	20	4·0		9	3·6	1·68*	(1·00)[k]	0·45°	0·44*
14.	*Iso*butylene						1·5°	2·05			3·5
15.	Vinyl ethyl ether	90		5°		3°	3°		3·0*		
16.	Allyl chloride	31[h]	41°	5·5°			4°				
17.	Allyl acetate	90	23°		5·5	5°	6°	1·2°[n]	0·6°	(1·00)*	
18.	Maleic anhydride	0·01°		6°		2·4°	10°			<0·008[j]	
19	Diethyl fumarate	0·30*		8°			12·2	0·12	0·011		(1·00)*
20.	Diethyl maleate	6·52*	20°	12°			13°	0·77*[f]	0·17*[g]		
21.	Trichloroethylene	16°	81°	67°		35°			0·66*		
22.	*Trans*-dichloroethylene	37							0·99*[h]		
23.	*Cis*-dichloroethylene	210							6·3*[i]		
24.	Tetrachloroethylene	185		470°		190°			6·8*		

Since one monomer in each of the following pairs was tested with only one other monomer, data are not included in the above table :

M_1	r_1	M_2	r_2
Vinyl acetate	0·35	Vinyl bromide	4 5
Styrene	0·18°	Ethyl acid fumarate	0·25°
Styrene	0·13	Ethyl acid maleate	0·01°
Styrene	0·19	Fumaronitrile	0·00°
Styrene	0·19*	Maleonitrile	0·00°

See opposite page for notes.

being required for solution of the two unknowns. Within experimental error, these ratios in oil-phase polymerisations are found to be independent [1a] of the rate of polymerisation, the reaction medium,[1d, 3] conversion, regulators, and impurities, but they depend on temperature [1d] and apply only as long as the polymerisation proceeds by a free-radical mechanism.[1a] Emulsion copolymerisation seems to differ only in so far as the solubility of one monomer in water may reduce its effective concentration in the oil-phase.[4]

From a determination of the monomer reactivity ratios in two-component copolymerisations, it is possible to predict how three-component and four-component systems will behave. The excellent agreement between prediction and experiment [1e] gives strong support to the correctness of the fundamental assumption that the behaviour of a growing radical depends, for practical purposes, only on the terminal radical grouping.

Experimental Data.—Most of the experimental data which will be used in this paper are summarised in Table I. The monomer reactivity ratios are very sensitive to errors in analyses, particularly when the ratios are much larger or smaller than unity. The errors are usually within the range to be expected from ordinary elementary analyses [1d, k] but are larger when a high-boiling monomer is difficult to remove from a polymer, or when precipitation of polymer during polymerisation leads to erratic results.

Types of Copolymerisation.—There are two extreme types of copolymerisation, the "ideal". and the "alternating" types, but the great majority of copolymerisations exhibit features of both. In the ideal [5] type of copolymerisation, the relative reactivities of the two monomers are the same for both radical types and a random copolymer is formed. If the monomers are close together in reactivity, as with styrene-*p*-methoxystyrene,[6] the composition of the copolymer being formed at any instant will approximate the composition of the feed. If the reactivities differ significantly, as with styrene-butadiene, or greatly, as with styrene-vinyl acetate, then the more reactive monomer will tend to predominate or may (until consumed) practically exclude the other monomer from reacting. In any event, which monomer adds to a growing radical is independent of which added last; one monomer reactivity ratio is the reciprocal of the other, and the product of the two ratios is unity.

In the other extreme type of copolymerisation, a 1 : 1 copolymer is formed over a wide range of feeds, as in copolymers of maleic anhydride with stilbene,[7] styrene, and allyl acetate.[8] Each type of radical reacts only with the other kind of monomer, and an alternating copolymer results. Both monomer reactivity ratios are essentially zero and their product is zero.

[3] Nozaki, *J. Polymer Sci.*, 455.

[4] Smith, *J. Amer. Chem. Soc.*; 1946, 68, 2069; Fordyce *et al.*, *ibid.*, 1947, 69, 581, 695, 1903.

[5] Wall, *ibid.*, 1944, 66, 2050. [6] Walling and Mayo, this Discussion.

[7] Wagner-Jauregg, *Ber.*, 1930, 63, 3213.

[8] Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1946, 68, 1495.

* ° Indicates ratios which are considered accurate within ± 10 % (*) or which may be in error by more than 30 % (°). Other ratios may be in error by more than 10 % but less than 30 %.

† For example, for the copolymerisation of styrene and methyl methacrylate, the monomer reactivity ratio for the styrene radical is given in column (2), row 3 and the ratio for the methacrylate radical is given in column (3), row 2. Monomer reactivity ratios for radicals 1, 4, 5, 10, 11, 14-16, 18, 21-4 are either given by notes *a-j*, or are experimentally indistinguishable from zero.

a-j Other monomer reactivity ratio of each pair: (*a*) 1·39*, (*b*) 0·35*, (*bb*) 0·16*, (*c*) 0·76*, both ratios at 90°, (*d*) 0·65, (*e*) 1·78, (*f*) 0·01, (*g*) 0·043°, (*h*) 0·086, (*i*) 0·018, (*j*) < 0·13, data at 35° of Bartlett and Nozaki, ref. 8.

k Alfrey and Harrison, *J. Amer. Chem. Soc.*, 1946, 68, 299.

l-n Calculated from data of Moffett and Smith, U.S. Patent 2,356,871, (*l*) 80°, (*m*) 45°, (*n*) 40°.

Most copolymerisations lie between these extremes: there is a general *average activity* of monomers in copolymerisation on which is superimposed a tendency for the monomers to alternate in copolymerisation.[1b] For most systems, the *products* of the monomer reactivity ratios lie between zero (for perfect alternation) and unity (for ideal copolymerisation). None of the systems mentioned in this paper has an r_1r_2 product significantly greater than one, i.e. independent polymerisation of the monomers may occur consecutively (as with styrene-vinyl acetate), but not simultaneously. Products of monomer reactivity ratios are thus a convenient measure of alternation tendency but they have the limitation that many monomer reactivity ratios are experimentally indistinguishable from zero and comparison of their products is then impossible.

The Average Activity of Monomers toward Radicals.—The monomers in Table I are listed in order of decreasing average activity toward radicals. The monomer reactivity ratios are the reciprocals of the relative reactivities toward the reference radical, the reactivity of the reference monomer being taken as unity in each column. The reciprocals of the listed ratios, when multiplied by the absolute rate constant for the reaction of the reference radical with the reference monomer, become the absolute rate constants for the reactions of the reference radical with the various monomers, but until the necessary factors become available,[9] the ratios or reactivities in one column cannot be compared with those in another column.

The monomers are divided into two groups, the 1- and 1 : 1-substituted ethylenes, and the 1 : 2-substituted ethylenes. Only the first group of monomers will be considered here. The ratios are seen to increase fairly uniformly in each column but there are a few exceptions. Many of the significant deviations are due to the high reactivity of a " donor " radical with an " acceptor " monomer or vice versa, to be considered later.

Table I shows that, on the whole, the monomers with conjugated vinyl, phenyl, carbonyl, nitrile and carbalkoxy groups are considerably more reactive towards free radicals than the monomers without such conjugation. The data show also that additional 1-methyl or 1-chlorine substituents increase the reactivities of the double bonds : * methacrylate is more reactive than acrylate ; methacrylonitrile is more reactive than acrylonitrile ; methallyl compounds are more reactive than allyl compounds ; vinylidene chloride is more reactive than vinyl chloride. These observations will now be considered in connection with other free-radical addition reactions of ethylene bonds.

Analogies with Other Addition Reactions.—In additions of hydrogen bromide, mercaptans, bisulphite, and certain organic halides,[10] such as carbon tetrachloride, by a free-radical chain mechanism, it is now commonly assumed [10, 11] that the bromine atom, mercaptan radical, sulphite ion radical, or trichloromethyl radical adds to the ethylene bond so that the more stable free radical is formed, stabilisation being effected by the conjugated or hyperconjugated group. From this explanation, it follows from the structures of abnormal hydrogen-bromide addition products [11] that phenyl, carboxyl, halogen and alkyl groups are more effective than hydrogen in stabilising a free radical, and that carboxyl, bromine and chlorine are more effective than methyl.

The same considerations of radical stability must apply to polymerisation reactions : monomer units should be attacked by a polymer radical so that the new radical is the more stable one. Assuming this analogy with simple addition reactions, the copolymerisation experiments then

[9] Burnett and Melville, *Nature*, 1945, **146**, 661 ; Swain and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 2381.

* These same conclusions have also been established recently by Nozaki.[8]

[10] Kharasch, Jensen and Urry, *ibid.*, 1947, **69**, 1100 ; Kharasch, Reinmuth and Urry, *ibid.*, 1105.

[11] Mayo and Walling, *Chem. Rev.*, 1940, **27**, 351.

show that in a competition between two different monomers for the same polymer radical, the monomer which can yield the more stable radical is the more reactive monomer. Thus structures of simple addition products indicate the structures of polymers; relative reactivities in copolymerisation indicate relative average reactivities in simple addition reactions. So far as data are available, both kinds of experiments yield the same order of radical stabilities.

Although abnormal additions of hydrogen bromide are commonly reported to give 100 % of one product within experimental error, some of the other isomer must also be formed.[12] Since the experimental errors are of the order of 1-5 %, product compositions indicate that the differences in free energies of activation for the two modes of addition of a bromine atom to an unsymmetrical olefine is at least 2-4 kcal./mole, a value consistent with the expected differences in stabilities of the radicals. By analogy, we should expect that a similar proportion of head-to-head addition should accompany the predominant head-to-tail addition in polymerisation, a conclusion recently reached by Flory from degradation studies.[13]

Reactivities of Double Bonds and Derived Radicals.—The substituents which lend the most stability to the resulting radical might be expected also to lend the most stability, and lowest reactivity, to the double bond in the unreacted monomer; but since these conjugated double bonds are actually more reactive, the conjugation and hyperconjugation which stabilise both the monomer and radical must contribute more to the stability of the activated complex than to the stability of the monomer and possibly of the radical as well. Only in this way can we account for the observation that less activation energy is required to convert a resonance-stabilised double bond to a resonance-stabilised radical than to convert an unstabilised double bond to an unstabilised radical. This concept will receive considerable support from a comparison of *cis* and *trans* isomers.

The conclusion that the most reactive double bonds yield the least reactive radicals and that the least reactive double bonds yield the most reactive radicals accounts qualitatively for some other phenomena in polymerisation. When a mixture of styrene and vinyl acetate polymerises,[1f] the vinyl acetate acts as an almost inert diluent for the styrene, and a little styrene inhibits the polymerisation of vinyl acetate. Although the unreactive styrene (substituted benzyl) radical can add readily enough to the reactive double bond in styrene, it adds only 1/50th as fast to the unreactive double bond in vinyl acetate, and although the reactive vinyl acetate (α-acetoxyalkyl) radical adds readily enough to the unreactive vinyl acetate double bond, it reacts 50-100 times as fast with the more reactive styrene double bond. Thus, a small proportion of styrene is able to pick up the reactive radicals, and convert them to unreactive benzyl radicals. These grow only very slowly in vinyl acetate and the probability of chain termination with another radical before chain growth occurs is greatly increased.

It may now be pointed out why there is no correlation between the average activity series of monomers in copolymerisation and the rates of polymerisation of monomers alone.[1m] The copolymerisation series compares the reactivity of two monomers toward a common radical; in single polymerisations, any increase in the reactivity of a double bond is more or less balanced by a decrease in the reactivity of the radical which is adding (and being formed), but the major difficulty in the use of overall rates of polymerisation is that they are highly dependent on the rate and mechanism of chain termination.[14]

[12] Mayo and Dolnick, *J. Amer. Chem. Soc.*, 1944, **66**, 985.
[13] Flory, *J. Polymer Sci.*, 1947, **2**, 36.
[14] Bartlett and Altschul, *J. Amer. Chem. Soc.*, 1945, **67**, 812, 816.

The Effect of Temperature on Copolymerisation.—Table II summarises some careful measurements on the temperature coefficients of monomer reactivity ratios.[14] Since each ratio is the quotient of two rate constants, changes with temperature give the differences in heats and entropies of activation for the respective reactions, and the quotient of the frequency factors. Table II shows that the monomer reactivity ratios do not vary greatly with temperature. The energy of activation is the principal factor determining relative reactivities of monomers and in most instances differences in entropies of activation are not significantly different from zero. Table I shows that for most radicals the ratio of the largest to the smallest reactivity is in the range 100-1000. Thus, whether any two monomers will copolymerise with great ease or not at all depends

TABLE II.—HEAT AND ENTROPY OF ACTIVATION DIFFERENCES IN THE COPOLYMERISATION OF SOME MONOMER PAIRS.*

Radical Type.	r_1.		$\Delta H_1^{\ddagger} - \Delta H_2^{\ddagger}$. (cal./mole.).	$\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger}$. (E.U./mole.°).	P_1Z_1/P_2Z_2.
	60°.	131°.			
Styrene	0·520 ± 0·026	0·590 ± 0·026	480 ± 250	0·12 ± 0·68	1·06 ± 0·30
Methyl methacrylate	0·460 ± 0·026	0·536 ± 0·026	580 ± 280	0·19 ± 0·76	1·10 ± 0·34
Styrene	0·747 ± 0·028	0·825 ± 0·005	380 ± 140	0·54 ± 0·36	1·31 ± 0·16
Methyl acrylate	0·182 ± 0·016	0·238 ± 0·005	1020 ± 340	0·66 ± 0·86	1·39 ± 0·49
Styrene	6·52 ± 0·05	5·48 ± 0·56	−660 ± 480	1·87 ± 1·36	2·55 ± 1·26
Diethyl maleate	<0·01	—	—	—	—
Styrene	0·301 ± 0·024	0·400 ± 0·014	1070 ± 320	0·82 ± 0·82	1·50 ± 0·50
Diethyl fumarate	0·0697 ± 0·0041	0·0905 ± 0·0008	990 ± 290	−2·35 ± 0·73	0·31 ± 0·14
Styrene	0·742 ± 0·030	0·816 ± 0·015	360 ± 170	0·48 ± 0·43	1·27 ± 0·24
p-Chlorostyrene	1·032 ± 0·030	1·042 ± 0·015	35 ± 120	0·40 ± 0·32	1·22 ± 0·18

* $\Delta S_1^{\ddagger}$, $\Delta H_1^{\ddagger}$, $\Delta S_2^{\ddagger}$, and $\Delta H_2^{\ddagger}$ are respectively the entropies and heats of activation for the reaction of M_1, with M_1 and M_2, each radical in each pair being taken in turn as M_1, for the indicated calculation. P_1Z_1/P_2Z_2 is defined by

$$r_1 = \frac{P_1Z_1}{P_2Z_2} \exp. \left(\frac{-\Delta H_1^{\ddagger} + \Delta H_2^{\ddagger}}{RT} \right)$$

largely on a maximum difference of 3-5 kcal./mole in free energy of activation for two competing reactions of a free radical; the widest possible range in practical results may depend upon factors which are imperceptible or of secondary importance in most organic reactions. The relative reactivities of different double bonds are of the same order as the indicated reactivities of the two points of attack in a single unsymmetrical double bond, and for the same reason.

The Alternation Effect.—Two principal explanations have been advanced for the tendency of monomers to alternate in copolymerisation. Price [15] has proposed that substituents in ethylene derivatives tend to remove or supply electrons to the double bonds, or the free radicals derived from them, in the same manner that these substituents displace electrons in the benzene ring. The resulting charges on the double bond or trivalent carbon atom then increase the tendency for a negative radical to react with a positive double bond or vice versa. The other explanation

[15] Price, *J. Polymer Sci.*, 1946, **1**, 83.

proposes [6, 8] that the same factors which lead to formation of complexes between monomers such as maleic anhydride and styrene or stilbene, or between aromatic polynitro-compounds and aromatic hydrocarbons, lead to interactions between radicals and monomers. More specifically,[6] if the nature of the attacking radical and reacting monomer are such that one may reasonably transfer a single electron to the other, then the additional resonance forms available to the activated complex considerably increase its stability. Alternation then should be expected between monomers which can serve as electron donors and monomers which can serve as electron acceptors. Both schemes lead to parallel predictions: that the larger the difference in charge or donor-acceptor ability between two monomers, the greater will be the alternation tendency. Table III

TABLE III.—ALTERNATION TENDENCIES IN COPOLYMERISATIONS AS MEASURED BY PRODUCTS OF MONOMER REACTIVITY RATIOS.

	Vinyl acetate	Butadiene	Styrene	Allyl acetate	Vinyl chloride	Methyl methacrylate	Vinylidene chloride	Methyl acrylate	Methyl vinyl ketone	β-Chloroethyl acrylate	Methacrylonitrile	Acrylonitrile
Vinyl acetate												
Butadiene												
Styrene		1·08										
Allyl acetate	0·3											
Vinyl chloride	0·38		0·34									
Methyl methacrylate	<0·03		0·26									
Vinylidene chloride	<0·1	0·19	0·16			0·61						
Methyl acrylate			0·14									
Methyl vinyl ketone			0·10									
β-Chloroethyl acrylate			0·054	<0·3					0·8			
Methacrylonitrile			0·05			0·43						
Acrylonitrile	0·25		0·02		0·06	0·24	0·34			1·1		
Diethyl fumarate	0·004		0·02		0·06		0·56					

gives qualitative support to these ideas: here the monomers have been arranged largely in order of increasing tendency to alternate with styrene. It then appears that alternation tendencies between other monomers are fairly consistent; the greater is the separation between two monomers in the series, the greater is their alternation tendency (the smaller is the r_1r_2 product).

An attempt has been made to treat the electrostatic effect on a quantitative basis [16] and to describe the general behaviour of each monomer in copolymerisation on the basis of its average or general activity, Q, and its polarity factor, e. However, the differences in tendencies of monomers to alternate with styrene and vinyl acetate, for example, indicate inconsistencies which may be difficult to account for. Further, data on the behaviour of *cis* and *trans* isomers cannot be accounted for by a simple electrostatic scheme but point to individual differences which become exaggerated in activated complexes. Other aspects of the quantitative proposal will be considered elsewhere.[6]

The Effects of Substituents on Average Activity and Alternation Tendencies of Ethylene Derivatives.—Using data in Tables I-III, the following rough estimate of the abilities of substituents, R—, to increase the average reactivity of the monomer, $H_2C{=}CHR$, toward free radicals is presented: *

$$C_6H_5— > H_2C{=}CH— > R—CO— > N{\equiv}C— > RO—CO— > Br— > Cl— > R—O—,\ R—CH_2— > H\ (?)$$

[16] Alfrey and Price, *J. Polymer Sci.*, 1947, **2**, 101.

* The position of Br depends entirely on the copolymerisations of vinyl acetate and vinyl bromide. In comparison with vinyl chloride, vinyl bromide shows a greater tendency to enter the copolymer and less tendency toward alternation.

The abilities of the same substituents to act as electron donors fall roughly in the order

$$R—O— > H_2C{=}CH— > C_6H_5— > R—CH_2— > H\ (?) > Br— > Cl— > R—CO—,\ R—O—CO— > N{\equiv}C—$$

There is no obvious relation between the two series. These series are a restatement and correlation of experimental observations. When two monomers are similar in electron donor-acceptor ability, then they form a random copolymer of which the initial composition depends on the average activities of the two monomers: if they are close together (e.g. styrene-butadiene) the composition of the copolymer approaches the composition of the feed; if they are quite different (e.g. styrene-vinyl acetate) then very little of the less reactive monomer enters the co-polymer initially. When two monomers differ widely in donor-acceptor properties, then there is a strong tendency for the monomers to alternate in co-polymerisation. If the monomers are similar in average activity (e.g., styrene-acrylonitrile), the composition of the copolymer will be close to 1 : 1 from a considerable range of feeds, but if the two monomers differ considerably in average activity (e.g. acrylonitrile-vinyl acetate) then the alternation effect may be obscured by the predominance of the more reactive monomer.

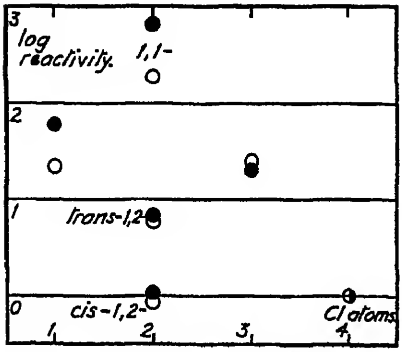

FIG. 1.—Logarithms of relative reactivities of chlorinated ethylenes, referred to tetra-chloroethylene as unity, toward radicals from vinyl acetate (solid circles) and styrene (open circles) as a function of the number of chlorine atoms.

Comparison of the behaviour of 1- and 1 : 1-substituted ethylenes indicates that the effects of substituents in both series are roughly additive. The effect of 2-substitution will be considered next.

The Effects of Symmetrical and Unsymmetrical Substitution on Reactivity.—Fig. 1 summarises the relative reactivities of all the chlorinated ethylenes[19] with the vinyl acetate- and styrene-type radicals. To make the results more easily comparable, the reactivity of tetrachloroethylene has been taken as unity in each series, and the actual reactivities of *cis*- and *trans*-dichloroethylenes and of tetrachloroethylene have been divided by two since they contain two equivalent positions capable of reacting. The high reactivities of vinyl and vinylidene chloride show clearly the activating effects of additional 1-substitution in vinyl chloride and the deactivating effects of 2-substitution in both of these monomers. The effects of additional 1-substitution were accounted for in connection with the discussion of average activity. The effects of 2-substitution must be largely steric: substituents in that position are closest to the point which must be attacked by the approaching radical. The possibility that the 2-chlorine atoms reduce the stability of the activated complex because they are less able than a 2-hydrogen atom to stabilise the 1-radical by hyperconjugation has been considered, but if we accept this explanation, then, since trichloroethylene is only one-third as reactive as vinyl chloride with the vinyl acetate radical, not significantly different with the styrene radical, we are forced to the improbable conclusion that the resonance effect of a 2-chlorine atom on a 1-radical is greater than the effect of a 1-chlorine atom on a 1-radical. Although substitution of a third chlorine atom in the 1 : 2-dichloroethylenes increases their reactivity, it is of interest that the differences between the *cis* and *trans* forms is larger than the difference between

the *trans* form and the trichloro-compound. These relations bring up the problem of accounting for the differences between *cis* and *trans* isomers, to be considered in the next section.

In copolymerisations with vinyl acetate, the products of the monomer reactivity ratios for vinyl chloride, *cis*-dichloroethylene, *trans*-dichloroethylene and vinylidene chloride are 0·38, 0·11, 0·085, and $< 0{\cdot}01$, respectively. This series shows that 2-substitution increases the alternation tendency of vinyl chloride with vinyl acetate, even though it decreases the total reactivity. Accordingly, the effects of 2-substitution on reactivity, as shown in Fig. 1, might be still larger if they were not partially compensated by the increased tendency of the more chlorinated monomers to alternate with styrene or vinyl acetate.

In the copolymerisation of monomers containing donor substituents with 1 : 2-disubstituted monomers containing strong acceptor substituents, then the donor-acceptor effect of the 2-substituent may be able to compensate fully for the normal deactivation by 2-substitution. Toward the styrene-type radical, e.g. diethyl fumarate is 2·5 times as reactive as methyl acrylate, and fumaronitrile is twice as reactive as acrylonitrile. When the reactivities of the disubstituted monomers are divided by two to allow for their two equally probable points of attack, the net result of 2-substitution on reactivity is very small. Toward the vinyl acetate radical, fumaric ester seems to be about ten times as reactive as acrylic ester, but the acrylate is more reactive toward radicals which are poorer donors (Table I).

Comparison of *Cis* and *Trans* Isomers.—Table IV summarises the relative reactivities of some geometrical isomers toward some reference radicals.[14] The table shows that diethyl fumarate is 6-20 times as reactive as diethyl maleate with the three reference radicals tested, but since maleic

TABLE IV.—RELATIVE REACTIVITIES OF SOME *Cis* AND *Trans* ISOMERS.

Reference Radical.	Isomer Pair.	More Reactive Isomer (Factor).	Less Stable Isomer.	Planar *cis* Form Hindered.
Styrene	Diethyl fumarate and maleate (*cis*)	*trans* (21X)	*cis*	+
Styrene	Ethyl acid fumarate and maleate	Insignificant difference	*cis*	?
Styrene	Fumaronitrile Maleonitrile	Insignificant difference	*cis*	—
Styrene	1 : 2-Dichloroethylenes	*trans* (6X)	*trans*	—
Vinyl chloride	Diethyl fumarate and maleate	*trans* (6·5X)	*cis*	+
Vinyl acetate	Diethyl fumarate and maleate	*trans* (15X)	*cis*	+
Vinyl acetate	1 : 2-Dichloroethylenes	*trans* (6·5X)	*trans*	—
Maleic anhydride	Stilbenes	*trans* (1·5-2X)	*cis*	+

anhydride is much more reactive than fumarate with styrene (the only radical for which reliable data are available), the low reactivity of maleate cannot be due to a general low reactivity of *cis* derivatives. Our earlier conclusion that resonance stabilisation of the activated complex by conjugated substituents is a crucial factor in reactivity provides a satisfactory explanation for these observations. In diethyl maleate, the size and position of the ester groups is such that both cannot lie in the plane of the rest of the molecule and the probability that either ester group will be coplanar is apparently small, but only a coplanar group can contribute to the resonance stabilisation of the activated complex. In maleic anhydride, however, *both* conjugated carbonyl groups are fixed in a position

where they can make the maximum contribution to the reactivity of the ethylene bond. Diethyl fumarate is an intermediate case.

In general, we would anticipate that the less stable isomer of a pair (the one present in smaller proportion in the equilibrium mixture) might be the more reactive one, since both isomers on reaction presumably are converted through very similar (at most, stereoisomeric) intermediates to the same radical. Tests of other pairs of isomers give qualitative support to this expectation.

In the half-esters, where one substituent is smaller and there is a possibility, at least, of internal hydrogen bonding, no significant difference between the maleate and fumarate was found. Apparently the higher energy of the *cis* form is compensated by a more favourable steric configuration of the *trans* form. In the corresponding nitriles, where there can be no interference between nitrile groups, and where the equilibrium mixture contains about 75 % *trans* isomer, again no significant difference was found between the reactivities of the two isomers. In the dichloroethylenes, where the equilibrium mixture contains about 78 % *cis* form, the less stable *trans* form is 6-7 times as reactive as the *cis* form. In the copolymerisation of maleic anhydride with the stilbenes, both isomers give essentially a 1 : 1 copolymer from a wide range of feeds and comparison has been made on the basis of *rates* of the two copolymerisations, assuming only (1) that the rate of chain initiation was the same in both reaction mixtures (with the same proportion of benzyol peroxide), and (2) that both isomeric stilbenes were converted to the same free radical. The relative reactivities suggest that both phenyl groups may lie in the plane of the rest of the molecule in *trans*-stilbene, but only one is *iso*stilbene, and that the number of coplanar phenyl groups may determine the number of points of attack.

Quantitative considerations bring out some additional points of interest. Comparison of the compositions of the equilibrium mixtures and relative reactivities of the dinitriles (3 : 1 *trans*, equally reactive) with styrene and of the dichloroethylenes with both styrene and vinyl acetate (3·5 : 1 *cis*, *trans* 6-7 times as reactive) shows that the differences in free energy of activation are not equal to the differences in free energy of formation, and therefore, that the two isomers do not react through the same activated complex, although they presumably yield the same radical eventually. The results suggest further that the details of interatomic relations which determine relative stabilities of monomers play an even larger role in determining the stabilities of the activated complexes. Finally, if overall dipole moment were important in determining reactivities of the dinitriles and dichlorides with donor radicals, then the *cis* forms should be more reactive in both cases, but if the net removal of electrons by these substituents were important, then the *cis* and *trans* forms should be equally reactive. Since the results are consistent with neither expectation, we conclude, for the present, that we are not yet able to interpret quantitatively the reactions of free radicals with ethylene bonds with these concepts.

Summary.

Study of the compositions of copolymers formed from known feeds permits determination of the relative reactivities of monomers toward the free radicals which occur in vinyl polymerisations. Accumulated data show that, on the average, terminal ethylenic bonds with conjugated unsaturation are most reactive because the conjugated groups reduce the activation energy required for reaction. Other substituents have smaller activating effects. Superimposed on this general effect of substitution is a tendency of many monomer pairs to alternate in copolymerisation. While this effect can be correlated qualitatively with the abilities of the respective substituents to accept or supply electrons, there is evidence that still other factors must be involved. These conclusions are supported by a comparison of the behaviours of *cis* and *trans* isomers and of the effects of symmetrical and unsymmetrical substitution on reactivity.

Résumé.

Les compositions des copolymères, formés à partir de proportions connues, permettent de déterminer les réactivités relatives des monomères envers les radicaux, produits dans les polymérisations vinyliques. De nombreux résultats montrent que, en moyenne, les liaisons éthyléniques terminales conjuguées sont les plus réactives, parce que les groupes conjugués réduisent l'énergie d'activation, nécessaire à la réaction. D'autres substituants ont des effets activants moins marqués. A cet effet général de la substitution, il s'ajoute une tendance de nombreuses paires de monomères à alterner en copolymérisation.

Zusammenfassung.

Die Untersuchung der Zusammensetzung von Kopolymeren, die aus bekannten Zusammensetzungen der Ausgangsstoffe gebildet werden, gestattet die Bestimmung der relativen Reaktivitäten von Monomeren für die freien Radikale, die in Vinylpolymerisationen entstehen. Angesammelte Daten zeigen, dass, im Durchschnitt, Endäthylenbindungen mit konjugierter Unsättigung die höchste Reaktivität besitzen, weil die konjugierten Gruppen die zur Reaktion nötige Aktivierungsenergie verringern. Andere Substituenten üben kleinere Effekte aus. Ausser diesem allgemeinen Substitutionseffekt besteht bei vielen Monomerpaaren eine Tendenz, in der Kopolymerisation mit einander abzuwechseln und ausserdem existieren Anzeichen dafür, dass noch andere Faktoren beteiligt sein müssen. Diese Folgerungen werden durch den Vergleich des Verhaltens von *cis*- und *trans*-Isomeren und den Einfluss von symmetrischer und unsymmetrischer Substitution auf die Reaktivität unterstützt.

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THE EFFECT OF SUBSTITUTION ON THE REACTIVITY OF THE STYRENE DOUBLE BOND TOWARDS FREE-RADICAL ATTACK: THE NATURE OF THE "ALTERNATING EFFECT" IN COPOLYMERISATION.

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One of the most interesting aspects of the new knowledge of the relative reactivities of olefinic double bonds which has sprung from copolymerisation studies lies in the finding that such relative reactivities depend, not only upon the olefin, but upon the attacking radical as well. Thus, the summary of data from these laboratories [1] shows that at least two major effects can be differentiated: first, a general order of monomer reactivity and, second, a specific tendency of certain monomers to "alternate" in copolymerisation. The first of these appears to be independent of the nature of the attacking radical and to parallel the expected contribution of resonance stabilisation of the product radical to the stability of the transition state. It thus arises in the same manner as the factors determining the direction of addition of free radicals to the double bond, e.g. the "abnormal" addition of hydrogen bromide.[1a, 2] The second factor appears to arise from differences in polarity or electron donor-acceptor properties of radical and double bond, and is of peculiar interest since it is without parallel among previously known free-radical reactions.

[1] (*a*) Mayo, Lewis and Walling, *Trans. Faraday Soc.* (*b*) Mayo, Lewis and Walling, *J. Amer. Chem. Soc.*, 1947, 69.
[2] Mayo and Walling, *Chem. Rev.*, 1940, 27, 351.

This paper summarises the results of extensive series [3] of copolymerisations of substituted styrenes and α-methylstyrenes with representative monomers with which they show negligible, weak, and strong tendencies to alternate in copolymerisation. These series were carried out in the hope of obtaining a clearer insight into the nature of the "alternating effect" in copolymerisation, since the effect of *meta-* and *para-*substituents on the resonance possibilities of the benzene ring and upon electron availability in the benzene side chain are comparatively well understood.

Experimental.

Description of specific experiments (all carried out at 60° in absence of air and presence of benzoyl peroxide catalyst), calculations of relative reactivities, and determination of experimental errors are all given elsewhere.[3] In most of the systems studied, however, reproducibility of experiments lay within the limits of the expected scatter of polymer analyses upon which the determination of monomer reactivity ratios depend. Results are thus as good as can be hoped for with our present techniques.

In copolymerisations of substituted styrenes with styrene and with methyl methacrylate [3a, b] relative reactivities were calculated directly from the measured monomer reactivity ratios. In the case of maleic anhydride-α-methylstyrene systems, however,[3c] all polymers consist almost entirely of regularly alternating α-methylstyrene and maleic anhydride residues, and all monomer reactivity ratios are essentially zero.[4] Accordingly, recourse was had to the competitive reaction between two α-methylstyrenes and maleic anhydride. Under such conditions, as long as any maleic anhydride remains, virtually the only reaction by which either α-methylstyrene enters the polymer is by reaction with a maleic anhydride type radical, and the reaction follows the law:

$$d[M_1]/d[M_2] = k_1[M_1]/k_2[M_2] \quad . \quad . \quad . \quad . \quad (1)$$

where M_1 and M_2 are the two α-methylstyrenes and k_1/k_2 the ratio of rate constants for the reaction of the two styrenes with the maleic anhydride type radical and thus the desired measure of relative reactivity.

The effects of substitution on the reactivity of the styrene (or α-methylstyrene) double bond towards attack by the styrene, methyl methacrylate, and maleic anhydride type radicals are listed in Table I. Monomer reactivity ratio products (r_1r_2's) which serve as qualitative measures [1] of the alternating tendencies for the copolymerisations, are also included for the first systems.[5]

Effect of Substitution upon Reactivity of Styrenes.—The effects of *meta-* and *para-*substitution upon reaction rates and equilibria in a wide variety of reactions of the sort proceeding through polar intermediates have been surveyed by Hammett [6] who has found that, in general, they obey quite well the law:

$$\log k/k_0 = \sigma\rho \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k and k_0 are rate or equilibrium constants for the side-chain reaction of the substituted and unsubstituted benzenes, σ is a parameter for each substituent (e.g. the *p*-methyl group) and ρ a parameter depending only upon the reaction (e.g. rate of hydrolysis of benzoyl chlorides). In order to see what, if any, sort of relationship exists between the effects of substituents on the reactivities of the styrene double bond in free-radical reactions and the known effects of substituents on polar reactions, in Fig. 1 logarithms of relative reactivities of the substituted styrenes and α-methylstyrenes taken from Table I are plotted against the Hammett σ-values for the substituents.

[3] (*a*) Walling, Briggs, Wolfstirn and Mayo, *J. Amer. Chem. Soc.* (in press). (*b*) Walling, Briggs and Wolfstirn, *ibid.* (*c*) Walling, Seymour and Wolfstirn *ibid.*

[4] The change from a series of styrenes to a series of α-methylstyrenes in maleic anhydride work was made to simplify analytical procedures and the determination of relative reactivities.[3c] The assumption made, that nuclear substituent have the same effect upon the reactivity of α-methylstyrene as upon styrene appears well borne out by the experimental results.

[5] The r_1r_2 products for maleic anhydride systems cannot be compared since they are indistinguishable from zero (probably $\leq 10^{-4}$).

[6] Hammett, *Physical Organic Chemistry* (McGraw-Hill Book Co., Inc., New York, 1940), Ch. VII.

Considering first reactivities of the substituted styrenes towards the unsubstituted styrene radical (black circles), a radical derived from a monomer showing no tendency to alternate with styrene, a close relation between relative reactivities and Hammett σ-values for the substituents is observed. In fact the systems obey eqn. (2) quite exactly, with a median deviation of points from the best straight line (drawn by the method of least squares) of only 0·024 log units, less than the average experimental error, and better than all but six of the 52 polar reactions originally compiled by Hammett.[6] In short, this radical reaction behaves like an ordinary polar reaction with a ρ-value (the slope of the line through the black circles) of 0·51, approximately the same as that for the ionisation of phenylacetic acids.[6,7] Since Hammett σ-values can probably be most simply interpreted as measures of the effect of substituents on electron density

TABLE I.—RELATIVE REACTIVITIES OF SUBSTITUTED STYRENES TOWARDS INDICATED RADICALS

Substituent.	Styrene.	Relative Reactivity[a] Methyl Methacrylate.	Maleic Anhydride.[b]
p-OCH_3	0·86 ± 0·08	1·59 ± 0·16	18·5 ± 0·1
	(0·95)[a]	(0·093)[a]	—
p-$N(CH_3)_2$	0·98 ± 0·06	2·24 ± 0·22	300
	(0·85)	(0·023)	—
p-CH_3	—	1·14 ± 0·06	1·72 ± 0·12
	—	(0·178)	—
m-CH_3	—	0·87 ± 0·04	—
	—	(0·26)	—
none	1·00	1·00	1·00
	(1·00)	(0·24)	—
p-F	—	—	0·72 ± 0·10
	—	—	—
p-Cl	1·35 ± 0·06	1·11 ± 0·05	0·79 ± 0·02
	(0·76)	(0·37)	—
p-Br	1·44 ± 0·04	1·16 ± 0·05	0·73 ± 0·15
	(0·69)	(0·44)	—
p-I	1·61 ± 0·13	1·28 ± 0·10	—
	(0·76)	(0·34)	—
m-Cl	1·56 ± 0·13	0·98 ± 0·15	—
	(0·70)	(0·43)	—
m-Br	1·82 ± 0·10	0·96 ± 0·04	0·96 ± 0·14
	(0·58)	(0·56)	—
p-CN	3·57 ± 0·35	2·09 ± 0·20	0·96 ± 0·57
	(0·325)	(0·31)	—
p-NO_2	5·20 ± 0·5	—	—
	(0·218)	—	—

[a] Quantities given in parentheses under relative reactivities are monomer reactivity ratio products.

[b] Relative reactivities for substituted α-methylstyrenes against α-methylstyrene.

at the site of reaction (here the styrene double bond), differences in reactivity might here be ascribed to changes in polar interaction between radical and monomer. A second source of the differences might be small variations in the contributions of the resonance structures of the product radicals which might, in turn, follow a Hammett series, or else a combination of the two. However, since the chief purpose of this paper is a discussion in the much larger effects observed in reactivity of substituted styrenes towards the radicals derived from more strongly alternating monomers, a more detailed discussion is given elsewhere.[3a]

Reactivities of substituted styrenes towards the methyl methacrylate type radical, derived from a monomer showing a moderate tendency to alternate with styrene ($r_1r_2 = 0·24$), are indicated in Fig. 1 by half-black circles. For

[7] Kindler, *Annalen*, 1927, **452**, 90.

the points on the right (styrene and the negatively-substituted styrenes) a reasonable agreement with a Hammett series is observed, and a line corresponding to a ρ-value of 0·33 for the reaction may be drawn through the points with a median deviation of 0·04 log units. On the other hand, the three points on the left (corresponding, from the left, to the substituents p-OCH_3-, p-$N(CH_3)_2$-, and p-CH_3-) show markedly increased reactivities and no relation to the usual order for polar reactions. These points also, it should be noted, correspond to monomers showing markedly increased alternating tendencies with methyl methacrylate (r_1r_2 values of 0·18 to 0·02).

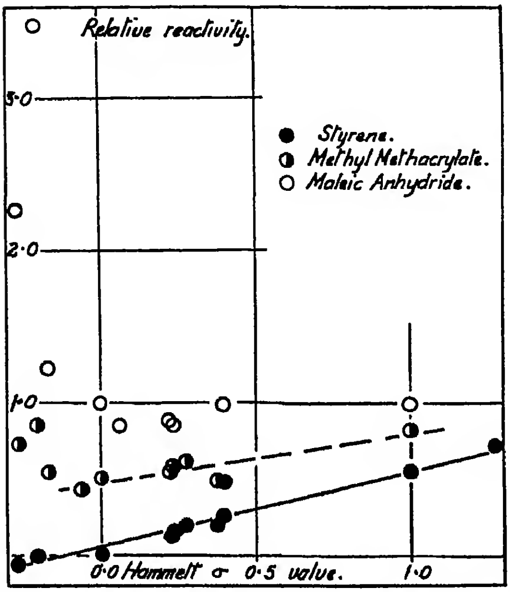
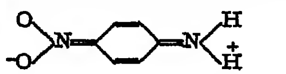
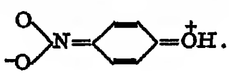


FIG. 1.—Relative reactivities of substituted styrenes towards indicated type radicals against Hammett σ-valuesof substituents. Position of ordinate scale is arbitrary.

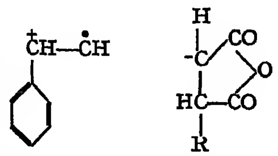
Reactivities towards the maleic anhydride radical, derived from a very strongly alternating monomer ($r_1r_2 < 10^{-4}$), are indicated in Fig. 1 by the open circles. In this reaction, it may be seen that the semblance to a Hammett series has been quite lost with p-CH_3, p-OCH_3 and p-$N(CH_3)$ groups producing greatly increased reactivity in that order, and p-halogen the lowest reactivities of all. In short, as one considers the effects of substitution on the reactivity of styrenes towards a series of radicals derived from monomers showing increasing tendency to alternate in copolymerisation with styrene, one finds a transition from an order of effects of substituents paralleling those observed in polar reactions and rather small in magnitude (about a six-fold change in going from p-OCH_3 to p-NO_2) to a quite different order and much greater magnitude of effect (several hundred-fold between p-$N(CH_3)$ and p-F). The possible origin of this phenomenon will be considered next.

The Nature of the Alternating Effect.—As we have seen in the previous section, the effect of nuclear substitution on the reactivity of styrenes towards carbonyl-conjugated radicals shows little relation to the Hammett series which governs most polar side-chain reactions of benzene. Accordingly, it appears most unlikely that the major source of the great tendency of all styrenes to react with such radicals, and, conversely of styrene radicals to react with such monomers (the familiar "alternating effect") can arise from any simple "electrostatic" or "polar" interaction between radical and double bond.[8, 9] In reactions proceeding through polar intermediates, deviations from the Hammett series can sometimes be accounted for by a consideration of special resonance forms available in the transition state, product, or reactants. Thus, for example, it has been found necessary to assign a second, larger σ-value to the p-nitro group when considering reactions of amines and phenols,[6] presumably because of additional contributions of resonance structures of the type,

 and .

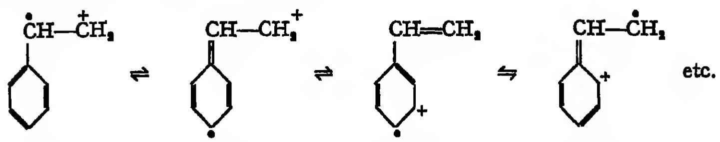
[8] Price, *J. Polymer Sci.*, 1946, 1, 83.
[9] Alfrey and Price, *ibid.*, 1947, 2, 101.

Similarly, the effects of *p*-alkyl groups on the rates of solvolysis of benzhydryl halides [10] has been interpreted in terms of resonance forms involving hyperconjugation between the carbonium ion and hydrogens of a *p*-methyl group. Here it seems plausible to employ a similar approach and, since electron-accepting and -donating properties of carbonyl-conjugated and aromatic systems, respectively, are well established, to consider contributions to the transition state in which an electron has been donated from the double bond of styrene to the carbonyl-conjugated radical.[11]

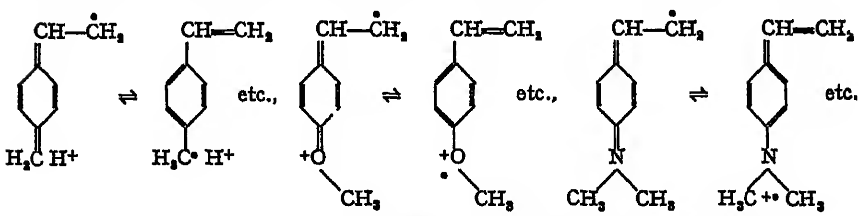


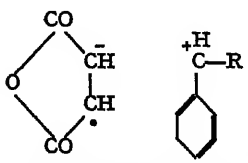
For the case of styrene-maleic anhydride, the resulting structures would be of the type shown in above equation.

Considerable stability might be expected from such a structure, for not only has the maleic anhydride portion become a relative stable enolate ion, but the styrene portion has available to it some 26 more-or-less equivalent structures of the types

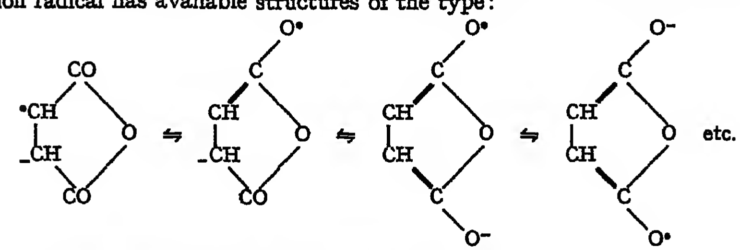


Qualitatively, this picture is also able to account for the increased reactivity towards carbonyl-conjugated radicals produced by the introduction of *p*-CH_3, *p*-OCH_3, and *p*-$N(CH_3)_2$ groups. Each introduces the possibility of a number of additional structures, e.g.





Similar contributions from polar resonance structures in the transition state are possible in the attack of the styrene radical on the conjugated double bond as shown opposite, where the substituted benzyl carbonium ion may distribute its charge to the *ortho-* and *para-*positions and the maleic anhydride enolate-ion radical has available structures of the type:

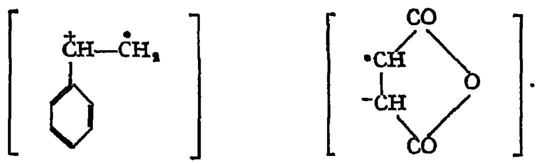


[10] Hughes, Ingold and Taher, *J. Chem. Soc.*, 1940, 949.

[11] The possibility that special resonance forms in the transition state were important in producing alternation in copolymerisation was first made to us by Prof. Saul Winstein of the University of California at Los Angeles, and we are indebted to him for several discussions helpful in formulating the viewpoint expressed here.

This formulation, incidentally, shows clearly why maleic anhydride, having two carbonyl groups over which to distribute its charge and odd electron, shows a greater alternating tendency than methyl methacrylate with one, and is in accord with the explanation given previously [1, 12] of the lower reactivity of a *cis* isomer such as diethyl maleate in which, due to steric interference, resonance may occur with not more than one carbonyl group at a time. Thus this concept of polar resonance forms can be made to account for both the conjugate reactions in an alternating copolymerisation.

Relation to Complex Formation.—An instructive analogy exists between the resonance forms available in the transition states of an alternating copolymerisation postulated in the previous section, and the structures proposed by Weiss [13] for the coloured molecular compounds formed between aromatic compounds and carbonyl-conjugated systems.[14] These consist of pairs of radical ions [15] in which an electron has been donated from the aromatic to the conjugated system, e.g. for styrene-maleic anhydride, a hybrid of the resonance structures available to



Since the halves of this structure correspond to the olefin portions of the polar forms of the transition states for the two reactions in the copolymerisation of styrene with maleic anhydride, a parallel should be anticipated between the effect of substituents on complex formation and on reactivity with carbonyl-conjugated monomers.[14] Some observations on such complexes are listed in Table II in which the nature of light absorption of complexes of substituted styrenes with maleic anhydride, 1 : 3 : 5-trinitrobenzene, and chloranil is compared with their reactivity towards the methacrylate radical. Maleic anhydride yields rather unstable complexes, highly dissociated in solution and, since all are yellow in dilute solution, their relative absorption of violet light has been compared. Chloranil complexes are more stable and have absorption maxima in the visible spectrum, while trinitrobenzene complexes have intermediate properties. Examination of the data of Table II shows a very reasonable correlation between increasing depth of colour (shade or intensity) and reactivity, and lends good support to the idea of the importance of the structures proposed for the transition state in alternating copolymerisations.

The parallel between complex formation and reactivity among the substituted styrenes, and the visible formation of coloured complexes with maleic anhydride suggests the possibility that alternating copolymerisations actually proceed through reaction of such complexes rather than the monomers themselves. If the point of view which we have advanced is correct, this would not upset our picture of the general nature of the forces producing alternation. However, since it is of importance to a detailed picture of the reaction and to an understanding of any kinetic studies, it is well to review the available evidence. Bartlett and Nozaki [14] have surveyed a number of monomer pairs, including the

[12] Lewis and Mayo, *J. Amer. Chem. Soc.* (in press).

[13] Weiss, *J. Chem. Soc.*, 1942, 245.

[14] A relation between the complex-forming and copolymerising tendencies of maleic anhydride has been suggested by Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1946, 68, 1495. Also, Woodward, *ibid.*, 1942, 64, 3058, has suggested structures similar to those of Weiss in the transition state of the Diels-Alder reaction.

[15] The formulation of Weiss [13] for molecular compounds as pairs of radical ions implies that they possess paramagnetic properties and should, accordingly, be susceptible to experimental test.

strongly alternating systems allyl acetate-maleic anhydride and allyl acetate-diethyl maleate, for evidence of association (chiefly by vapour pressure measurements) with negative results. A similar investigation of the systems styrene-methyl methacrylate by Dr. Lewis [16] in this laboratory employing viscosity measurements and thermal analysis also have yielded no evidence of complex formation. Another approach to the problem is through kinetic studies.

TABLE II.—COMPLEXES OF SUBSTITUTED STYRENES.

Substituent.	Relative Reactivity.[c]	Maleic Colour.	Anhydride Intensity.[a]	Trinitrobenzene Colour.	Chloranil Colour.
p-OCH_3	1·59	yellow	3·95	orange	red-violet
p-$N(CH_3)_2$	2·24	red [b]	20·5	deep violet	sky blue
p-CH_3	1·14	yellow	0·202	deep yellow	orange
m-CH_3	0·87	,,	0·080	yellow	—
None	1·00	,,	0·027	,,	yellow
p-Cl	1·11	,,	0·046	,,	,,
m-Cl	0·98	,,	0·019	pale yellow	—

[a] Log I_0/I for a 10 mm. cell containing 1 M. styrene and 1 M. maleic anhydride in chloroform viewed with a Corning 511 (violet) filter.
[b] Yellow in dilute soln.
[c] Towards the methyl methacrylate type radical.

For the systems styrene-methyl methacrylate and stilbene-maleic anhydride (which both gives a completely alternating copolymer and forms a stable complex with a dissociation constant of about 0·05), Dr. Lewis [16] has found no clear evidence of complex participation. For styrene-maleic anhydride the kinetic order is high, but so far too erratic for any clear-cut decision. Finally, studies by Nozaki [17] and in this laboratory [18, 19] have shown no effect of dilution with an inert solvent upon the monomer reactivity ratios of styrene-methyl methacrylate, such as would be expected if an unstable complex contributed to the alternating tendency within this pair. In short, many monomer pairs between which no evidence of compound formation are found alternate in copolymerisation, and no cases exist where complex participation can be clearly demonstrated.

Application of the Alfrey-Price Equation to Copolymerisations of Substituted Styrenes.—Although the arguments given above have led us to the conclusion that the "alternating effect" in copolymerisation arises primarily from the availability of special resonance forms to the transition state rather than electrostatic interaction between radical and double bond, it seems of interest to see how our data may be fitted to the equation of Alfrey and Price.[9] In fact, our data make a particularly good test of its validity since a comparison of the reactivities of a series of substituted styrenes avoids the difficulties of changes in steric hindrance and entropy of activation occasioned by changing of groups at the site of reaction. According to the treatment of these authors, the behaviour of any monomer in copolymerisation may be described by two parameters Q, related to its general activity, and e, a polarity factor, which are related in turn to the monomer reactivity ratios by the expressions :

$$r_1 = Q_1/Q_2 \,.\, \exp. {}^{-e_1(e_1 - e_2)}, \quad r_2 = Q_2/Q_1 \,.\, \exp. {}^{-e_2(e_2 - e_1)} \qquad . \quad (3)$$

In Table III, Q's and e's have been calculated for a number of substituted styrenes, using our data [3a] for copolymerisations with styrene. Then, using Alfrey and Price's values of Q and e for styrene and methyl

[16] Unpublished work. [17] Nozaki, *J. Polymer. Sci.*, 1946, **1**, 581.
[18] Mayo and Lewis, *J. Amer. Chem. Soc.*, 1944, **66**, 1594.
[19] Walling, Lewis, Cummings, Briggs and Mayo, *ibid.* (in press).

methacrylate, we have determined the expected relative reactivities of the same substituted styrenes towards the methacrylate radical. Although some qualitative agreement is obtained, calculated and measured reactivities differ in general by more than the experimental error of the measurements, and we are led to the peculiar conclusion that halogen substituents lower the general reactivity of styrene.

In systems in which the relative reactivities of two monomers towards the radical from a third are compared (e.g. maleic anhydride-two α-methylstyrenes) the Alfrey-Price equation takes the form :

$$k_1/k_2 = Q_1/Q_2 \exp. {-e_3(e_1 - e_2)} \qquad . \quad . \quad . \quad (4)$$

where k_1/k_2 is the same ratio of rate constants appearing in eqn. (1) and e_3 is the polarity factor for maleic anhydride. If the reasonable assumption is made that a nuclear substituent has the same effect on Q and e for

TABLE III.—CALCULATION OF RELATIVE REACTIVITIES OF SUBSTITUTED STYRENES TOWARDS THE METHYL METHACRYLATE RADICAL.

Substituent.	Q.	e.	Relative Calc.	Reactivity Found.
p-OCH_3	1·08	−1·226	1·08	1·59
p-$N(CH_3)_2$	1·48	−1·404	1·48	2·24
None	1·00	−1·00	1·00	1·00
p-Cl	0·800	−0·476	0·800	1·11
p-Br	0·783	−0·391	0·783	1·16
p-I	0·955	−0·476	0·955	1·28
m-Cl	0·860	−0·403	0·860	0·98
m-Br	0·869	−0·262	0·869	0·96
p-CN	1·39	0·060	1·39	2·09

α-methylstyrene as for styrene itself, using eqn. (4), a value of e_3 may be calculated for each relative reactivity measurement in the last column of Table I for which the corresponding Q and e are available in Table III. Results are listed in Table IV, and may be seen to give a wide scatter. Further, not only must e_3 be at least two for compatibility with the measured maximum value of ($r_1r_2 < 10^{-4}$) for styrene-maleic anhydride, but e_3 values near zero lead to the implausible conclusion that the polar properties of maleic anhydride are the same as methyl methacrylate and vinylidene chloride. In summary, in our opinion, our data fail to give any quantitative support to an equation in the form of that proposed by Alfrey and Price.

TABLE IV.—CALCULATION OF "POLARITY FACTOR" FOR MALEIC ANHYDRIDE.

Substituent used.	Polarity Factor.
p-OCH_3	11·0
p-$N(CH_3)_2$	13·2
p-Cl	0·23
p-Br	0·11
m-Br	−0·14

Applications to Other Systems.—Our use of the idea of polar forms in the transition state of a radical reaction to interpret the "alternating effect" in the copolymerisation of styrenes and carbonyl-conjugated olefins infers immediately that they are important in other alternating systems as well. Accordingly, it is encouraging to note that the empirical electron-donor series deduced from other copolymerisation studies falls in the same order ; RO— > alkyl > H > halogen, as the effect of substituents on the reactivity of α-methylstyrenes towards maleic anhydride. Such a result is entirely plausible, since the groups should be even more effective in providing additional resonance structures when attached directly to the radical or double bond than when their effects are transmitted through

the benzene ring. In fact, it should be noted that the importance of polar forms to free-radical reactions need be in no way a peculiarity of copolymerisations, but may well occur in other free-radical reactions, in particular attack of other free-radicals on double bonds. Although the only evidence available at present, the direction of addition to unsymmetrical bonds, points to the primary importance of stability of the product radical rather than any electron donor-acceptor effect,[3] the possibility in other reactions should certainly be worth investigation, preferably, in view of the complexities of free-radical kinetics, through competitive reactions.

Summary.

By means of copolymerisation experiments, relative reactivities have been determined for a series of substituted styrenes towards the styrene and methyl methacrylate-type radicals and for a series of α-methylstyrenes towards maleic anhydride.

Towards the styrene type radical-substituents produced effects similar to those encountered in polar reactions. However, in reactions with the carbonyl conjugated radicals, derived from monomers which alternate in copolymerisation with styrene, effects of substituents follow a different order and parallel the tendencies of the styrenes to form complexes with carbonyl-conjugated compounds.

This result is discussed and it is concluded that the " alternating effect " in copolymerisation arises from the presence in the transition state of polar structures similar to those arising in molecular compounds.

Résumé.

Par des expériences de copolymérisation, on a déterminé les réactivités relatives pour une série de styrènes substitués par rapport au styrène et aux radicaux du type méthacrylate de méthyle et pour une série de α-méthylstyrène par rapport à l'anhydride maléique. Envers le radical du type styrène, les substituants produisent des effets semblables à ceux rencontrés dans les réactions polaires. Cependant, dans les réactions avec des radicaux carbonyle conjugués, dérivés de monomères qui alternent avec le styrène dans la copolymérisation, les effets des substituants suivent un ordre différent et ont les mêmes tendances que les styrènes à former des complexes avec les composés carbonyliques conjugués. On discute ce résultat et on conclut que " l'effet alterné " dans la copolymérisation provient de la présence, dans l'état de transition, de structures polaires, semblables à celles qui se présentent dans les composés moléculaires.

Zusammenfassung.

Mit Hilfe von Kopolymerisationsversuchen sind die relativen Reaktivitäten von einer Reihe von substituierten Styrolen für Radikale vom Styrol- und Methylmethacrylattypus und von einer Reihe von α-Methylstyrolen für Maleinsäureanhydrid untersucht worden. Für die Radikale vom Styroltypus war der Effekt von Substituenten ähnlich wie bei polaren Reaktionen. Hingegen verläuft in Reaktionen mit den konjugierten Karbonylradikalen, die von Monomeren, die in der Kopolymerisation mit Styrol abwechseln, herstammen, der Effekt von Substituenten in einer anderen Reihenfolge und parallel zur Tendenz der Styrole, mit den konjugierten Karbonylverbindungen Komplexe zu bilden. Dieses Ergebnis wird erörtert und es wird geschlossen, dass der " Abwechslungseffekt " bei der Kopolymerisation auf die Gegenwart im Übergangszustand von polaren Strukturen, ähnlich wie die bei Molekularverbindungen auftretenden, zurückzuführen ist.

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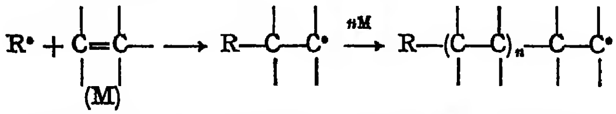
THE INFLUENCE OF STRUCTURE ON THE RELATIVE REACTIVITY OF FREE RADICALS IN POLYMERISATION SYSTEMS.

By Charles C. Price.

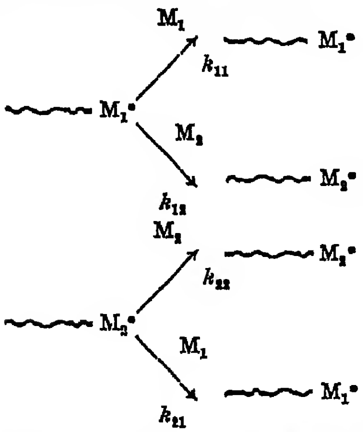
Received 14th July, 1947.

It has been established and is now generally accepted that the usual vinyl polymerisations of monomers such as styrene, acrylates and vinyl halides, initiated by peroxidic catalysts, by light or by heat, proceed through a free-radical chain reaction:



It is thus possible to interpret much of the experimental data obtained from studies of various polymerisation systems in terms of the relative reactivity of various free radicals toward monomers and other molecules which may be present in the reaction medium. It is the purpose of this paper to present such an interpretation, qualitatively or quantitatively as the data permit, from results of studies of copolymerisation, inhibition, retardation, chain transfer and chain initiation.

1. Copolymerisation.—Mayo [1] was one of the early investigators to realise the important information on relative reactivity of free radicals which could be obtained from experimental data on copolymerisation. The copolymerisation ratios, r_{12} and r_{21}, in the copolymerisation equation, derived independently and almost simultaneously by Mayo,[1] by Wall [2] and by Alfrey and Goldfinger,[3] are measures of the relative reactivity of monomers M_1 and M_2 to the two free radicals derived from addition of a radical to these two monomers.



$$\frac{dM_1}{dM_2} = \frac{(M_1)}{(M_2)}\left(\frac{r_{12}(M_1) + (M_2)}{r_{21}(M_2) + (M_1)}\right)$$

$$r_{12} = k_{11}/k_{12}$$
$$r_{21} = k_{22}/k_{21}.$$

Since the values of r_{12} and r_{21} can be established by studying the composition of copolymer (dM_1/dM_2) formed at various initial monomer concentrations ((M_1) and (M_2)), one can thus obtain quantitative information

[1] Mayo and Lewis, *J. Amer. Chem. Soc.*, 1944, **66**, 1594. Mayo, Lewis and Hulse, *ibid.*, 1945, **67**, 1701.
[2] Wall, *ibid.*, 1944, **66**, 2050.
[3] Alfrey and Goldfinger, *J. Chem. Physics*, 1944, **12**, 205.

on the tendency of free radicals derived from different monomers to add to the double bond of these monomers. For example, Mayo, Lewis and Hulse [1] have made a careful study of the copolymerisation of all possible pairs among the four monomers, acrylonitrile, methyl methacrylate, styrene and vinylidene chloride. The data are summarised in Table I, expressed in terms of the relative reactivity of the different monomers to any radical end-group.

TABLE I.—DATA OF MAYO, LEWIS AND HULSE ON RELATIVE RATES OF MONOMER ADDITION TO VARIOUS RADICALS.

Monomer \ Radical	Styrene.	Acrylonitrile.	Methyl Methacrylate.	Vinylidene Chloride.
Styrene	(1·0)	25·0	2·0	7·0
Acrylonitrile	2·5	(1·0)	0·8	2·7
Methyl methacrylate	2·0	7·0	(1·0)	4·1
Vinylidene chloride	0·5	1·1	0·4	(1·0)

One of the qualitative conclusions immediately obvious from perusal of even these limited data is that the reactions of such highly-reactive intermediates as the free radicals involved as intermediates in polymerisation may nevertheless be highly specific and selective. Thus, e.g., the relative rates of addition of a free radical to the olefin bond of styrene and of acrylonitrile may vary by a factor of 62·5 depending on whether that free radical may be one derived from styrene or acrylonitrile. This *selective* factor in copolymerisation was qualitatively recognised from the phenomenon of heteropolymerisation, involving the successful polymerisation of two monomers, such as maleic anhydride and stilbene or fumarates and simple olefins, neither of which would polymerise successfully alone. It is thus obvious that, to account for such observations, there must be a selective factor greatly promoting addition of one radical to the second monomer and the second radical to the first monomer. This factor has been interpreted on the basis of polarity in the radical and the monomer.[4, 5]

In addition to this selective polar factor, there is another important influence on the copolymerisation tendency related to the general ease with which a given radical will add to a particular double bond, regardless of polarity. Mayo [6] has presented extensive experimental data in support of this factor and has termed it the " general monomer reactivity " factor. He has further pointed out that it seems to be closely related to the possibilities for resonance stabilisation of the radical adduct formed.

A third important factor to consider is the steric one. This must sometimes be of considerable importance, particularly for monomers substituted at both ends of the double bond, such as maleic anhydride, stilbene, maleates and fumarates, and may even be of some importance in monomers containing two bulky substituents at one end of the double bond, such as α-methylstyrene, 1 : 1-diphenylethylene and even methyl methacrylate.

It has recently been possible, at least for those cases where steric factors are not disturbing, to derive an equation for the copolymerisation ratios

[4] Price, *J. Polymer Sci.*, 1946, 1, 83; *Mechanisms of Reactions at the Carbon-Carbon Double Bond* (Interscience, New York, 1946).

[5] Alfrey and Price, *ibid.*, 1947, 2, 101.

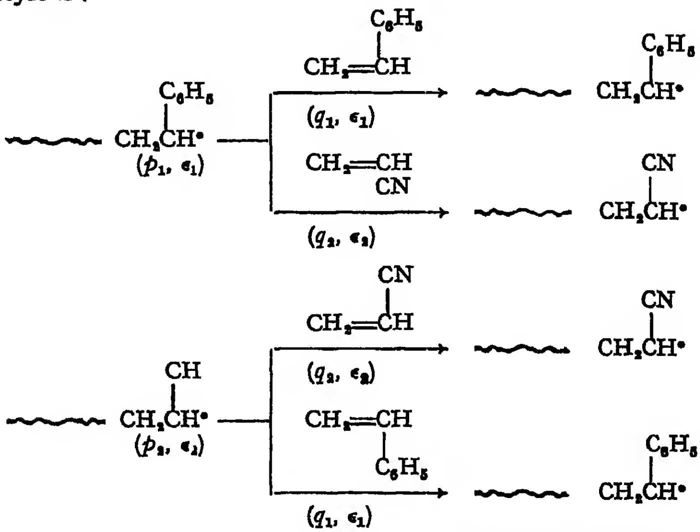
[6] Papers presented at symposia on *Mechanisms of Organic Reactions* at Notre Dame in September, 1946, and on *Copolymerisation* at the Polytechnic Institute fo Brooklyn, December, 1946.

expressing the "selective" or "polar" factor (e_1 or e_2) and the "general monomer reactivity" factor (Q_1 or Q_2) in more precise terms.[6]

$$r_{12} = k_{11}/k_{12} = Q_1/Q_2 e^{-e_1(e_1 - e_2)} \quad . \quad . \quad . \quad (1)$$

$$r_{21} = k_{22}/k_{21} = Q_2/Q_1 e^{-e_2(e_2 - e_1)} \quad . \quad . \quad . \quad (2)$$

These equations were derived from the expression for a rate constant on the basis of the assumption that the activation energy could be split into an "energy" factor and an "electrical" factor.[7] The latter is considered to be a simple coulombic charge interaction between charges ϵ_1 and ϵ_2. The former is considered to be composed of two pieces, related to the free energy of the polymer radical (p_1 or p_2) and of the monomer double bond (q_1 and q_2). We might illustrate for the case of acrylonitrile and styrene:



Eqn. (1) and (2) may be derived on the basis of the assumption that the free energy of activation for the four processes indicated above may be split into (1) factors (p_1 or p_2) associated with either radical plus (2) factors (q_1 or q_2) related to the ease with which a neutral radical could add to either monomer double bond plus (3) factors ($\epsilon_x\epsilon_y/rD$) expressing the interaction of charge between that donated to the radical carbon by the substituent attached to it (phenyl or nitrile group) and that donated to the double bond by the substituent attached to it. The simplifying assumption has been made that the charge donated by a particular substituent to a double bond is the same as that donated to a radical carbon atom by the same substituent. The success with which the equation based on this assumption can be applied seems ample justification that this is indeed a satisfactory approximation. One may then write the rate constants k_{11} and k_{12} as follows:

$$k_{11} = \alpha_{11} e^{-\Delta F_{11}/RT} = \alpha_{11} e^{-(p_1 + q_1 + \epsilon_1^2/rD)/RT} \quad . \quad . \quad (3)$$

$$k_{12} = \alpha_{12} e^{-\Delta F_{12}/RT} = \alpha_{12} e^{-(p_1 + q_2 + \epsilon_1\epsilon_2/rD)/RT} \quad . \quad . \quad (4)$$

If monomers one and two are such that no serious steric hindrance is involved in the addition reaction, α_{11} and α_{12} may be taken as the collision numbers and will be approximately equal. The ratio of k_{11} to k_{12}, or r_{12}, will then become:

$$r_{12} = \frac{e^{-q_1/RT}}{e^{-q_2/RT}} e^{-\epsilon_1(\epsilon_1 - \epsilon_2)/rDRT} \quad . \quad . \quad . \quad . \quad (5)$$

[7] See, e.g., Ri and Eyring, *J. Chem. Physics*, 1940, 8, 433; Price, *Chem. Rev.*, 1941, 21, 37.

At a given temperature one may set $e^{-q/RT} = Q$ and $\epsilon/\sqrt{rDRT} = e$ to obtain eqn. (1). Eqn. (2) may be derived in a similar fashion from expression for the rate constants k_{22} and k_{21}.

The values for Q and e for a number of monomers are summarised in Table II. The values for acrylonitrile, methyl methacrylate, styrene and vinylidene chloride are based on the excellent data of Lewis, Mayo and Hulse.[1] The other values are based in many cases on more fragmentary and less reliable data and are undoubtedly more subject to some experimental error.

It should be pointed out that, on the basis of eqn. (1) and (2), Q and e are not independent variables and unique values for e cannot be derived from any amount of data on copolymerisation ratios alone. The data in Table II are based on the assumption that the average charge on the four

TABLE II.—ALTERNATE VALUES FOR Q AND e WITH THE CHARGE FOR STYRENE CHOSEN AS −1·0 OR −0·7, RESPECTIVELY.

	Q.	e.	Q'.	e'.
Styrene	(1·0)	(−1)	(1·0)	(−0·7)
Acrylonitrile	0·34	1	0·62	1·3
Methyl methacrylate	0·64	0	0·86	0·3
Vinylidene chloride	0·16	0	0·22	0·3
Vinyl chloride	0·1	0	0·14	0·3
Allyl chloride	0·03	−0·3	0·04	0
Methyl acrylate	0·35	0·5	0·55	0·8
Vinyl acetate	0·1	−0·6	0·13	−0·3
Butadiene	0·6	−0·6	0·77	−0·3
Dichlorostyrene	1·5	0·3	2·2	0·6
(Maleic anhydride	1·5	1·8	3·4	2·1)

monomers of Lewis, Mayo and Hulse [1] is zero. This seems to give fairly reasonable values for Q and e, in agreement with the qualitative concept that Q, the monomer reactivity factor, is related to resonance stabilisation and that e, the electrical factor, parallels the charge induced by a given substituent in the benzene ring. It seems likely that the zero point for e may lie as much as 0·3 of a unit lower than indicated in Table II (column 3). Values for Q' and e', recalculated on this basis, are included for comparison in the last two columns of Table II. The calculation involved is derived simply from eqn. (1) on the basis that Q_1 and Q'_1 will be assigned the same value. We may then rearrange eqn. (1) to express Q in terms of Q_n, $e_1 - e_n$ and Δe (where Δe is the change in assignment of the zero point for the e axis):

$$Q_n' = Q_n e^{-\Delta e(e_1 - e_n)}.$$

One might approximate the absolute magnitude of the charge ϵ from the value of the arbitrary parameter e since $e = \epsilon/\sqrt{rDRT}$. If we choose a value of r, the distance separating charges in the transition state, as 2 A.° or 2×10^{-8} cm., somewhat greater than a covalent carbon-carbon bond length, a dielectric constant of unity, a temperature of 298° K. and evaluate R in terms of ergs per molecule, this equation indicates that a unit value of e corresponds to a charge of about $0·3 \times 10^{-10}$ E.S.U. This charge is of the same order of magnitude as the charge induced by similar groups on the benzene ring, as estimated by Ri and Eyring [7] from rates of substitution on the basis of considerations very similar to those outlined above.

Since it seems reasonable to expect that the effect of substituents on the aromatic ring would be paralleled by effects of similar groups on an olefin bond, [7, 8] the values of e for various substituents or combinations of

[8] See, e.g., Allan, Oxford, Robinson and Smith, *J. Chem. Soc.*, 1926, 401.

substituents have been compared with estimated values of the charge induced by the group in the benzene ring. Since it seems likely that the charges on the carbon atom α to the substituent in the radical and β to it in the monomer will be those most concerned, we have used the *sum* of the charges on the *meta* and *para* carbon atoms for the purpose of comparison. The values are summarised in Table III and seem to indicate a definite parallelism between the charge a substituent gives a double bond (as estimated from rates of copolymerisation) and the charge it gives to the benzene ring, as measured by Hammett's σ constant.[9]

TABLE III.—COMPARISON OF VALUES OF e WITH CHARGES INDUCED IN BENZENE BY THE SUBSTITUENTS AT THE MONOMER DOUBLE BOND.

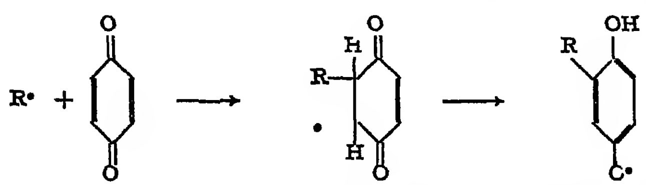
Monomer.	Substituents.	e.	$\sigma_m + \sigma_p$.
Styrene	C_6H_5	−1	−0·24[a]
Acrylonitrile	CN	1	1·68
Methyl methacrylate	CH_3 $COOCH_3$	0	1·08 − 0·24 = 0·84
Vinylidene chloride	Cl_2	0	1·20
Vinyl chloride	Cl	0	0·60
Allyl chloride	CH_2Cl	−0·3	0·74[b]
Methyl acrylate	$COOCH_3$	0·5	1·08
Vinyl acetate	$OCOCH_3$	−0·6	−0·15[c]
Butadiene	$CH{=}CH_2$	−0·6	−0·24[a]
Maleic anhydride	$(CO)_2O$	1·8	2·16

(*a*) Value for the methyl group.
(*b*) Estimated from Ri and Eyring's value for the charge induced.
(*c*) Value for the methoxyl group.

The qualitative concept of polarity as an influence in polymerisations can be extended to account for heteropolymerisations involving such unusual "monomers" as sulphur dioxide, oxygen and carbon monoxide.[4]

2. Inhibition and Retardation.—Since most inhibitors such as quinones and nitroaromatic compounds evidently exert their inhibitory action by adding a reactive free radical to give one less reactive to the monomer molecules,[4] the process involved would appear to involve the same factors as copolymerisation.

(resonance stabilised)



(semiquinone, resonance stabilised)

[9] Hammett, *Physical Organic Chemistry* (McGraw-Hill, New York, N.Y., 1940), p. 188.

In order for the substance to act as an effective inhibitor it must react rapidly with the radical. This would be promoted by high resonance energy in the adduct (large Q value) and as large a difference in polarity as possible (favourable electrical factor). Thus one might expect trinitrobenzene, with the strongly positive character of the ring carbons induced by the nitro groups, to be a more effective inhibitor of " negative " monomers (styrene) than of " positive " (acrylonitrile).

3. Chain Transfer.—In a chain-transfer process, where a molecule reacts with a polymer radical to produce a new radical capable of chain initiation, only the second step is regulated by the factors discussed under copolymerisation.

$$R^{\bullet} + CCl_4 \rightarrow RCl + {}^{\bullet}CCl_3$$

$$Cl_3C^{\bullet} + M \rightarrow CCl_3M^{\bullet}.$$

Thus, for carbon tetrachloride as a transfer agent, one would expect the second step, involving addition of the trichloromethyl radical with its odd electron on the strongly-positive carbon, to proceed most readily for a " negative " monomer double bond.

Although it seems profitable and useful to analyse the process of addition of a radical to a double bond in terms of electrical and general reactivity factors, the factors affecting the type of free-radical reaction represented in the first step of the transfer process above seems more difficult to understand. This reaction, attack of a radical to remove an atom such as a hydrogen or halogen, is of considerable general importance and one worthy of considerable thought and effort to elucidate the general principles governing it.

4. Chain Initiation.—One other free-radical reaction of great importance is that initiating a free radical chain reaction, such as polymerisation. This step involves first the generation of a radical fragment from the catalyst and then its addition to a monomer molecule. This second step should be regulated by the same general principles outlined above for other radical additions to a double bond. This problem seems readily amenable to experimental attack and such investigations are currently in progress at Notre Dame.

Résumé.

La plupart des résultats expérimentaux obtenus dans les polymérisations vinyliques de monomères peuvent être interprétés par les réactivités relatives de divers radicaux libres envers les monomères et les autres molécules présentes dans le mimieu de la réaction. On établit une équation pour déterminer les taux de copolymérisation en fonction du facteur polaire ou " sélectif " et de la " réactivité générale " du monomère. On discute qualitativement d'après cette équation les résultats des études d'inhibition, de retard, de transfert et de commencement de chaîne.

Zusammenfassung.

Es wird gezeigt, dass viele Versuchsdaten über die Vinylpolimerisation von Monomeren auf Basis der relativen Reaktivität von verschiedenen freien Radikalen für Monomere und andere Moleküle im Reaktionsgemisch erklärt werden können. Es wird eine Gleichung für die Kopolymerisationsbrüche als Funktionen der selektiven oder polaren Faktoren und der allgemeinen Monomerreaktivität abgeleitet. Ergebnisse der Untersuchung von Unterdrückung und Verzögerung, Kettenübertragung und Kettenbeginn werden in qualitativer Weise auf Basis dieser Gleichung besprochen.

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RATES OF RADICAL REACTIONS IN THE LIQUID PHASE.

I. ABSOLUTE VELOCITY CONSTANTS IN VINYL POLYMERISATIONS.

By C. H. Bamford and M. J. S. Dewar.

Received 11*th August*, 1947.

The determination of absolute velocity constants in radical reactions, and the quantitative study of radical reactivities are of great theoretical interest. The investigation of vinyl polymerisations is specially attractive in this connection, since their comparative simplicity and special features permit a detailed kinetic treatment. In general there are four velocity constants to be determined—initiation (k_1), propagation (k_2), transfer (k_3) and termination (k_4); two relations between these may be found by measuring the overall rate of polymerisation and the molecular weight of the product. Melville [1] and Bartlett [2] and their co-workers have used the rotating-sector method of Briers, Chapman, and Walters [3] to measure the life-time of a growing chain in the photopolymerisation of liquid vinyl acetate, and were able to determine k_2 and k_4. Their values for k_2 are in agreement, but those for k_4 differ by a factor of nearly 40. (For a possible explanation of this see Nozaki and Bartlett.[2])

A new method for determining all four velocity constants has been recently devised in this laboratory.[4] It depends on the use of viscosity measurements to follow the course of polymerisation. Similar measurements have been made before but their theoretical implications have not been realised.

Summary of Method.

The usual kinetic scheme involves unjustifiable simplifications. In the thermal (uncatalysed) or photo-polymerisation the first step must lead to the formation of a diradical, which will then propagate from both ends. On the other hand the transfer reaction produces a single radical growing at one end only. Therefore the initial polymer has twice the average molecular weight of the transfer polymer, and the kinetics need appropriate modification. The complete scheme for the thermal and photochemical polymerisation is given below.

$$\left.\begin{array}{lll}
2M \rightarrow 2X \text{ or } D_2 & k_1 & \multirow{2}{*}{\Big\}\text{Initiation.}} \\
M + h\nu \rightarrow 2X \text{ or } D_2 & AI & \\
X + M \rightarrow X & k_2 & \text{Propagation.} \\
D_2 + M \rightarrow D_1 + R & 2k_3 & \\
D_1 + M \rightarrow P_2 + R & k_3 & \text{Transfer.} \\
R + M \rightarrow P_1 + R & k_3 & \\
D_2 + X \rightarrow D_1 + Q & 2k_4 & \\
D_1 + X \rightarrow P_2 + Q & k_4 & \text{Termination.} \\
R + X \rightarrow P_1 + Q & k_4 & \\
2X \rightarrow 2Q & k_4 &
\end{array}\right\} \quad . \quad . \quad (1)$$

[1] Burnett and Melville, *Nature*, 1945, 156, 661; *Proc. Roy. Soc.*, 1947, 189, 456.
[2] Bartlett and Swain, *J. Amer. Chem. Soc.*, 1945, 67, 2273; Nozaki and Bartlett, *ibid.*, 1946, 68, 2377.
[3] Briers, Chapman and Walters, *J. Chem. Soc.*, 1926, 562.
[4] Bamford and Dewar, *Proc. Roy. Soc. A*, 1948, 192, 309.

X represents any active centre and Q any dead centre. D_2 is the initial polymer growing at both ends, D_1, that growing at one end only, and P_2 dead initial polymer. R and P_1 are growing and dead transfer polymer respectively. I is the light intensity and A a constant depending on the extinction coefficient and quantum yield. Only wave-lengths which are weakly absorbed are used ($\epsilon < 0{\cdot}05$) so that the rate of chain starting is sensibly constant throughout the liquid.

As we are interested in viscosity changes, it is necessary to know the relation between viscosity, molecular weight, and concentration. Using the relation of Schulz and Sing,[5] which we have confirmed for the polymers under discussion, it is possible to determine from the measured specific viscosity an " ideal " specific viscosity ($= c[\eta]$) which the solution would have if the specific viscosity were always proportional to the base molar concentration, c. Recent investigations have suggested that $[\eta]$ is given by an equation of the Houwink [6] type,

$$[\eta] = K\overline{M}^{\alpha} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which K, α, are constants for a given polymer-solvent mixture, and $\overline{M}$ the number average molecular weight. We have confirmed this equation for polystyrene solutions (see following paper).

Applying the stationary state method to eqn. (1) and using (2), we find :

$$\overline{M} = \frac{2k_2M_0(k_1k_4)^{\frac{1}{2}}}{2\beta + \xi} \quad . \quad . \quad . \quad . \quad (3)$$

$$\frac{d\eta}{dt} = KM_0^{\alpha}[M]^2\left(\frac{k_2^2}{k_4}\right)^{\frac{1}{2}(1+\alpha)}k_1^{\frac{1}{2}(1-\alpha)}\ \frac{\xi(\beta + 2^{\alpha}\omega\xi)}{(\beta + \xi)^{1+\alpha}} \quad . \quad . \quad (4)$$

where M_0 is the molecular weight of the monomer,

$$\beta = k_3(k_1k_4)^{-\frac{1}{2}}, \quad \xi = \left(1 + \frac{AI}{k_1[M]^2}\right)^{\frac{1}{2}}, \quad \omega = \frac{2 + \alpha}{2^{1+\alpha}}, \text{ and}$$

$\frac{d\eta}{dt}$ is the rate of increase of ideal specific viscosity during irradiation with light of intensity I.

Measurement of $d\eta/dt$ over a range of light intensities provides three relations between the constants, giving the values of β, $\left(\frac{k_2^2}{k_4}\right)^{\frac{1}{2}(1+\alpha)}k_1^{\frac{1}{2}(1-\alpha)}$ and A. (The experimental technique is thus greatly simplified since only relative light intensities need be measured.) A third relation between the velocity constants may then be obtained by measuring the molecular weight of a thermal or photo-polymer (eqn. (3)).

In order to obtain a fourth relation, and so to evaluate the constants absolutely, we make use of the fact that on cutting off the light the rate of polymerisation does not fall immediately to its dark value, but remains abnormally high for some time. The photochemical after-effect, $\Delta\eta_I^t$, may be defined as the difference between the observed ideal specific viscosity at time t and that calculated on the assumption that the rate falls instantaneously to the thermal value on interrupting the light. It may be shown that

$$\Delta\eta_I^t = \frac{nKM_0^{\alpha}[M]^{1+\alpha}k_2^{1+\alpha}}{2k_4^{1+\alpha}\beta^{\alpha}}\left[\int_{x_I^0}^{x_I^t}\left\{\frac{(2^{\alpha}\omega + \beta)(\lambda^m - x^m)x^{n-m-1}}{(\lambda^n - x^n)\lambda^{m+n}} + \frac{2^{\alpha}\omega - \beta}{\nu^n}\cdot\frac{x^{n-m-1}}{x^n - \nu^n}\right.\right.$$

$$\left.\left. - \frac{2^{\alpha}\omega + \beta}{\lambda^{m+n}}\cdot\frac{x^{n-1}}{x^n - \nu^n}\right\}dx + \frac{2\beta^2(2^{\alpha}\omega - 1)}{m\lambda^n\nu^n}\left\{\frac{1}{(x_I^t)^m} - \frac{1}{(x_I^0)^m}\right\}\right] \quad (5)$$

[5] Schulz and Sing, *J. prakt. Chem.*, 1943, 161, 161.
[6] Houwink, *ibid.*, 1940, 157, 15.

where $\alpha = m/n,\ \theta = [M]k_1^{\frac{1}{2}}k_4^{-\frac{1}{2}},\ \lambda^n = \beta + 1,\ \nu^n = \beta - 1$

and $$(x_I^t)^n = \left\{\beta + \frac{(\xi + 1) + (\xi - 1)e^{2[M]t(k_1k_1)^{\frac{1}{2}}}}{(\xi + 1) - (\xi - 1)e^{2[M]t(k_1k_1)^{\frac{1}{2}}}}\right\}.$$

As $t \to \infty$, the after-effect approaches a limit, $\Delta\eta_I^\infty$.

Experimental.

The monomers used in this work have to be of exceptional purity. Purification was effected in a high-vacuum system, by repeated distillation, and treatment with lithium, heat and ultra-violet light to remove all catalysts and inhibitors. The liquids were then distilled into quartz vacuum viscometers, which had been heated to bright redness under vacuum.

For each intensity a series of runs were carried out for different times of illumination (t). The total increase in viscosity is given by [7]

$$\delta\eta = at + \Delta\eta_I^t \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where a is the photochemical rate. Thus both a and $\Delta\eta_I^t$ were found.

Results.

So far we have studied only styrene and methyl methacrylate. It appears that with these monomers the kinetic scheme above is followed very closely. Fig. 1 shows the intensity-rate curve calculated from (4) together with the experimental points for methyl methacrylate at 0°. The agreement is very good

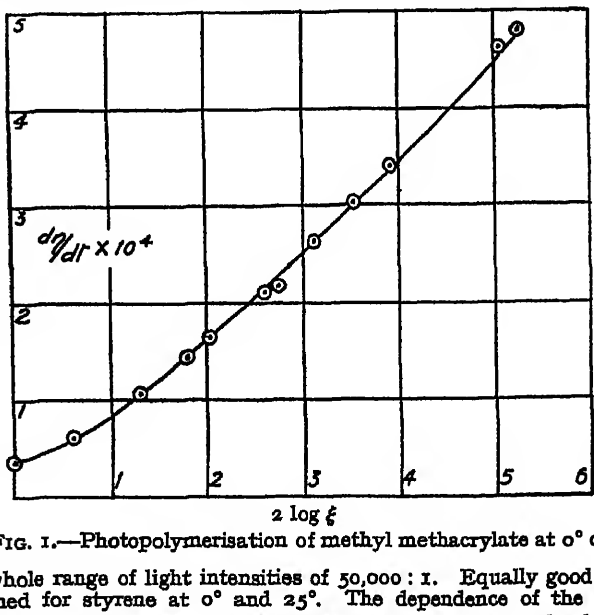

FIG. 1.—Photopolymerisation of methyl methacrylate at 0° C.

over the whole range of light intensities of 50,000 : 1. Equally good agreement was obtained for styrene at 0° and 25°. The dependence of the after-effect $\Delta\eta_I^t$ on t and I was also determined for styrene and agreed very closely with that calculated from eqn. (5). The main results are given in Table I. Table II shows the activation energies and frequency factors for styrene, with estimated maximum errors in the energies.

The values taken for K, α, will be discussed in the main paper.[4]

[7] Allowance must be made for the "pre-effect," due to the finite time taken for the stationary state to be established after the light has been turned on. The pre-effect vanishes at infinite intensity, and with the intensities used is never large. In practice the pre-effect is calculated from an expression similar to eqn. (5).

Discussion.

(i) We may compare the following values of the velocity constants with those given by Melville [1] and Bartlett [2] for vinyl acetate at 25° viz.

$$k_2 \sim 1000,\ k_4 = 3 \times 10^9\ \text{(M)},\ k_4 = 10^8\ \text{(B)}$$

From copolymerisation experiments it is known that for a given radical, the reactivity falls in the series, styrene > methyl methacrylate > vinyl

TABLE I.

	Styrene, 0°.	Styrene, 25°.	Methyl Methacrylate, 0°.
k_1	4.51×10^{-18}	1.32×10^{-15}	6.83×10^{-15}
k_2	6.91	18.7	41.6
k_3	7.47×10^{-5}	6.68×10^{-4}	6.13×10^{-4}
k_4	1.83×10^6	2.79×10^6	2.69×10^6
β	26	11	4.51
K	4.57×10^{-3}		5.05×10^{-4}
α	0.65		0.80
$\overline{M}$ (thermal)	9.44×10^6	2.78×10^6	5.93×10^6

TABLE II.

$E_1 = 37.0 \pm 2$ kcal. $\quad A_1 = 1.23 \times 10^{12}$
$E_2 = 6.5 \pm 1$ $\quad A_2 = 1.02 \times 10^6$
$E_3 = 14.2 \pm 1$ $\quad A_3 = 1.50 \times 10^7$
$E_4 = 2.8 \pm 1$ $\quad A_4 = 3.07 \times 10^8$

acetate. The relative values of the propagation constants therefore suggest that radical reactivities rise in the same series. This is consistent with current views, according to which the resonance energies of the radicals should rise in the series vinyl acetate < methyl methacrylate < styrene.

The low reactivity of the styrene radicals is reflected in the finite activation energy for termination, whereas Melville [1] states that termination in vinyl acetate is not activated. As a result of this, the life times of single radical and a growing polymer molecule, and a kinetic chain are surprisingly long. Values are given in Table III for styrene at several temperatures, and for methyl methacrylate at 0°.

TABLE III.

	Styrene.			Methyl Methacrylate 0°.
	0°.	25°.	100°.	
Life of one radical .	1.6×10^{-2}	6.2×10^{-3}	7.5×10^{-4} sec.	2.5×10^{-3} sec.
Life of growing polymer molecule . .	25 min.	2.8 min.	1.24 sec.	148 sec.
Life of kinetic chain .	11 hr.	33 min.	3 sec.	816 sec.

(ii) The value of E_1 for styrene is considerably greater than has been generally assumed. This is mainly due to the neglect of chain transfer by previous workers (cf. ref. 4 for fuller discussion). It is interesting that

the frequency factor is approximately normal, in conflict with the ideas of Harman and Eyring.[8] The other values are more or less what has been expected for the types of reaction concerned. Chain transfer certainly cannot be neglected in the thermal reaction. The number of times an initial radical centre undergoes transfer in a kinetic chain is β. This decreases with increasing temperature, but even at 100° has the value 1·6 according to our measurements.

(iii) The polymerisation of methyl methacrylate shows some peculiar features which make it difficult to study. We have found that irradiation of either the liquid or the vapour by ultraviolet light produces a catalyst, while an inhibitor is produced spontaneously on standing. The results obtained by Melville[9] can be interpreted readily in these terms, and it seems unnecessary to postulate non-terminating chains. A full account of this work will be published later.

Summary.

A method is described for determining the absolute velocity constants of initiation, propagation, chain transfer and termination in vinyl polymerisations. Results are given for styrene and methyl methacrylate. The reactivities of the radical intermediates are discussed in terms of their structures. Some peculiar features of the methyl methacrylate polymerisation are mentioned briefly.

Résumé.

On décrit une méthode qui permet de déterminer les constantes absolues de vitesse pour l'initiation, la propagation, le transfert de chaîne et la terminaison dans les polymérisations vinyliques. On indique les résultats pour le styrène et le méthacrylate de méthyle et l'on discute les réactivités des radicaux intermédiaires d'après leur structure.

Zusammenfassung.

Es wird eine Methode für die Bestimmung der absoluten Geschwindigkeitskonstanten fur Ketteneinleitung, -fortpflanzung, -übertragung und -abbruch in Vinylpolymerisationen beschrieben. Resultate für Styrol und Methylmethacrylat werden berichtet. Die Reaktivitäten der Radikalzwischenprodukte werden mit Bezug auf ihre Struktur besprochen.

[8] Harman and Eyring, *J. Chem. Physics*, 1942, 10, 557.
[9] Melville, *Proc. Roy. Soc. A.*, 1937, 163, 511.

II. RADICAL REPLACEMENT REACTIONS.

Mayo[1] established that when vinyl polymerisation is carried out in a solvent, the latter participates in chain transfer. Mayo showed that

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_0} + \frac{k'_3\phi}{k_2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\bar{P}$, $\bar{P}_0$ are the number average degrees of polymerisation, in solution and in pure monomer respectively, k'_3, k_2 are the velocity constants for chain transfer with solvent and propagation, and ϕ is the mole ratio solvent/monomer. The same equation follows from the more detailed kinetic scheme of the previous paper. The determination of k_2 (cf. previous paper) enables us to deduce k'_3 from the ratio k'_3/k_2 found by Mayo's method. Since the transfer reaction with the solvent is essentially a radical replacement we are thus able to determine absolutely the velocity

[1] Mayo, *J. Amer. Chem. Soc.*, 1943, 65, 2324.

constants of such reactions. Further, by finding the power of the intrinsic viscosity which must be substituted for $\bar{P}$ in (1), it is possible to evaluate α in the relation:

$$[\eta] = K\bar{M}^{\alpha} = KM_0^{\alpha}\bar{P}^{\alpha}. \quad . \quad . \quad . \quad . \quad (2)$$

If transfer takes place in a halogenated solvent, $\bar{P}$ may be determined by chemical end-group methods, and hence K also found.

Experimental.

Method.—Mixtures of redistilled styrene and solvent were heated in nitrogen-filled sealed tubes in thermostats at 60° and 80°, until about 5 % polymerisation had occurred. The polymers were isolated either by precipitation with a large

TABLE I.

	CCl_4.			CBr_4.		$CH_2Cl.CH_2Cl$.		$C_2H_4Br_2$.	
	60°.	80°.	100°.	60°.	80°.	60°.	80°.	80°.	100°.
k'_2	0·804	1·94	4·54[a]	159	282	$1·904 \times 10^{-3}$	$1·163 \times 10^{-2}$	$3·25 \times 10^{-2}$	0·1112
E	10·7			6·7		21·2		16·2	
A	$7·60 \times 10^{6}$			$3·92 \times 10^{6}$		$1·26 \times 10^{11}$		$2·99 \times 10^{8}$	

k'_2 in l. mol.$^{-1}$ sec.$^{-1}$ E in kcal. [a] Recalculated from data of Suess, Pilch and Rudorfer (ref. 3).

excess of methanol, or by vacuum distillation. Similar results were obtained by both methods. Intrinsic viscosities were determined in toluene at 25° using an Ostwald No. 1 viscometer, and extrapolated to zero concentration by the method of Schulz and Sing.[8]

Results.—In Fig. 1 values of $1/P$, calculated from (2) with $\alpha = 0·65$ $K = 4·57 \times 10^{-3}$, are plotted against ϕ, for styrene—CCl_4 mixtures at 60°. The points lie on a straight line within the limits of experimental error. This value of α was obtained by a more accurate graphical method which will be described elsewhere and the mean value of K found from chlorine estimations. Eqn. (2) with these values of α and K holds for polystyrenes with molecular weights in the range 10^3 to at least 10^6.

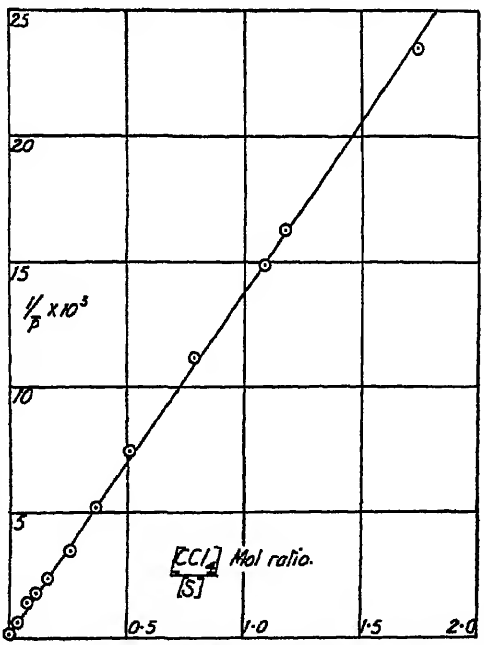

FIG. 1.—Molecular weights of polystyrenes prepared in carbon tetrachloride at 60° C.

These values were then used to determine $\bar{P}$ for other polymers by eqn. (2). From the results of the previous paper, the values of k_2 at 60°, 80°, 100°, and 120° may be calculated to be 59·0, 102·4,

[8] Schulz and Sing, *J. prakt. Chem.*, 1943, 161, 161.

168, and 262 l. mol.$^{-1}$ sec.$^{-1}$ Hence from (1) values of k'_3 may be found. These are given, together with activation energies and frequency factors, in Table I.

The figures calculated by Mayo [1] from the results of Suess *et al.*[3] need correction, as these authors used the Staudinger equation (i.e. (2) with $\alpha = 1$) for determining molecular weights. We have calculated the velocity constants, activation energies, and frequency factors in the cases where sufficient data are available. The results are given in Table II. We may mention that the drift in velocity constants noted by Mayo, and attributed by him to failure of the Staudinger equation for low molecular weights, is in fact due entirely to his use of the wrong exponent in eqn. (2).

TABLE II.

	Toluene.			Ethyl benzene.			Benzene.		*n*-Heptane.	Tetra-chlor-ethane.
	80°.	100°.	120°.	80°.	100°.	120°.	80°.	100°.	100°.	100°.
k'_3	$4{\cdot}15 \times 10^{-3}$	$1{\cdot}70 \times 10^{-2}$	$5{\cdot}89 \times 10^{-2}$	$1{\cdot}43 \times 10^{-2}$	$4{\cdot}06 \times 10^{-2}$	$1{\cdot}41 \times 10^{-1}$	$1{\cdot}57 \times 10^{-3}$	$6{\cdot}67 \times 10^{-3}$	$3{\cdot}89 \times 10^{-2}$	0·500
E	18·2			18·2			19·1			
A	$6{\cdot}68 \times 10^{8}$			$1{\cdot}60 \times 10^{8}$			$8{\cdot}79 \times 10^{8}$			

Discussion.

The results in this paper are preliminary in nature, and only tentative conclusions can be drawn from them. It seems to be established that the frequency factors vary over a considerable range—from $7{\cdot}6 \times 10^{6}$ in CCl_4 to $1{\cdot}26 \times 10^{11}$ in $C_2H_4Cl_2$. The rate of reaction increases in the series $CH_2Cl—CH_2Cl < CHCl_2—CHCl_2 < CCl_4$, as would be expected, since the chlorine substituent stabilises the radicals formed by transfer. Likewise toluene and ethylbenzene react more readily than benzene, since the former pair can give mesomeric benzyl radicals. Bromides react faster than the corresponding chlorides, possibly because the C—Br bond energy is less than that of C—Cl. The very high transfer constant with CBr_4—about three times the propagation constant—suggests that with quite moderate concentrations of CBr_4, P should become very small, i.e. simple addition should predominate. Kharasch *et al.*[4] have indeed obtained a 94 % yield of the addition compound $PhCHBr—CH_2CBr_3$, using a 6/1 molar ratio of halide to styrene. Incidentally this result confirms the general mechanism for chain transfer.

It is, however, surprising that the activation energy and frequency factor are so high in ethylene dichloride. The values given in Table I were calculated from our results at 60° and 80°; inclusion of Suess' results at 100° would give even higher values. The effect therefore appears to be genuine. It is also interesting that the activation energy for transfer with styrene (14·2 kcal.) given in the previous paper is considerably less than those for other benzene derivatives.

Summary.

Measurement of the degrees of polymerisation of polyvinyl compounds prepared in solution enables the velocity constant of the transfer reaction with the solvent to be evaluated in terms of the velocity constant of chain propagation

[3] Suess, Pilch and Rudorfer, *Z. physik. Chem. A*, 1937, 179, 361; Suess and Springer, *ibid.*, 1937, 181, 81.

[4] Kharasch, Elwood, Jenson and Urry, *J. Amer. Chem. Soc.*, 1947, 69, 1100; Kharasch, Reinmuth and Urry, *ibid.*, 1105.

(cf. Mayo [1]). Using values for the latter found in Part I, the absolute velocity constants of transfer have been calculated for styrene in a number of solvents. The transfer reactions are essentially radical replacements, and as such their rates are discussed in terms of the structure of the solvents. This work incidentally leads to an unambiguous method for establishing the relation between intrinsic viscosity and molecular weight of vinyl polymers.

Résumé.

On a calculé les constantes absolues de vitesse de transfert pour le styrène dans un certain nombre de solvants, en employant la constante de vitesse de propagation de chaîne, dont les valeurs ont été obtenues dans la partie I. Les réactions de transfert sont des remplacements de radicaux et on discute leurs vitesses d'après la structure des solvants, ainsi qu'une méthode sans ambiguité pour établir la relation entre la viscosité intrinsèque et le poids moléculaire des polymères vinyliques.

Zusammenfassung.

Die absoluten Geschwindigkeitskonstanten der Übertragung sind für Styrol in einer Reihe von Lösungsmitteln unter Benützung der im I. Teil erhaltenen Werte für die Geschwindigkeitskonstante der Kettenfortpflanzung berechnet worden. Die Übertragungsreaktionen sind Radikalersetzungen und ihre Geschwindigkeiten werden auf Grund der Struktur der Lösungsmittel erörtert. Eine unzweideutige Methode zur Feststellung der Beziehung zwischen der inneren Viskosität und dem Molekulargewicht des Polymeren wird besprochen.

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GENERAL DISCUSSION

Dr. G. Salomon (*Delft*) said : Although the series of relative reactivities explain a number of known facts on copolymerisation they will not permit one to predict the course of reaction for all combinations discussed in the paper by Mayo *et al.* It was found some years ago by Dr. v. d. Meer in our laboratory that isoprene acts as a powerful inhibitor on the polymerisation of vinylidene chloride, a result which could neither be predicted nor completely understood by present theory.

Dr. C. H. Bamford (*Maidenhead*) said: We have recently determined the absolute propagation constants for styrene, vinyl acetate, and methyl methacrylate. By using these in conjunction with Table I of Mayo, Lewis and Walling's paper, we obtain values (p. 318) for the absolute " propagation " constants at 60° c. for these radicals and a number of monomers.

The table on the next page is interesting in that it allows a quantitative comparison between the reactivities of a given monomer and the three radicals. (Obviously comparison of the figures in any one vertical column gives no information other than that which could be obtained from Mayo, Lewis and Walling's table alone). Two features may be mentioned.

(1) The general order of reactivity of the radicals is vinyl acetate > methylmethacrylate > styrene. This is the expected order (cf. Nozaki), the effectiveness of substituents in stabilising the radicals being in the order C_6H_5 >—COOMe ~ Me > MeCOO—.

(2) The very high values of the propagation constant of vinyl acetate radicals with styrene, methyl methacrylate, vinylidene chloride and diethyl fumarate are noteworthy. These approach the value normally associated with termination constants.

It is very gratifying to hear that Prof. Melville's values for methyl methacrylate agree with our own, and that he agrees with our view that a catalyst is produced by irradiation of methyl methacrylate. As regards the chemical nature of the catalyst we have no direct evidence, but incline to the view that it may be an active dimer. We are, however, working on this subject at present, and hope to be able to give our results later.

ABSOLUTE PROPAGATION CONSTANTS AT 60° C.

Monomer. / Radical.	Styrene.	Vinyl Acetate.	Methyl Methacrylate.
Butadiene	75		710
Styrene	59	$2 \cdot 6 \times 10^5$	386
Me methacrylate	114	$1 \cdot 8 \times 10^5$	177
Me vinyl ketone	203		
Methacrylonitrile	197		265
Acrylonitrile	147	$4 \cdot 3 \times 10^5$	131
β-Chloroethyl acrylate	109		
Methyl acrylate	79	$2 \cdot 6 \times 10^4$	
Vinylidene chloride	29·5	$2 \cdot 6 \times 10^5$	70
Methallyl chloride	2·7	$2 \cdot 0 \times 10^4$	24
Methallyl acetate	0·83		18
Vinyl chloride	3·5	$1 \cdot 1 \times 10^4$	14
Vinyl acetate	1·1	$2 \cdot 63 \times 10^3$	8·9
*Iso*butene			
Vinyl ethyl ether	0·66	$8 \cdot 8 \times 10^3$	
Allyl chloride	1·9		4·3
Allyl acetate	0·66	$4 \cdot 4 \times 10^3$	7·7
Maleic anhydride	5900		
Diethyl fumarate	197	$2 \cdot 4 \times 10^5$	
Diethyl maleate	9·1	$1 \cdot 5 \times 10^4$	8·9
Trichloroethylene	4·5	$4 \cdot 0 \times 10^3$	2·3
Trans-dichlorethylene	1·8	$2 \cdot 7 \times 10^3$	
Cis-dichlorethylene	0·26	$4 \cdot 2 \times 10^3$	
Tetrachloroethylene	0·32	$3 \cdot 9 \times 10^3$	

Perhaps I may mention one further feature of the methacrylate polymerisation, viz., the production of an inhibitor on warming, or even spontaneously on standing at room temperatures. When methyl methacrylate is irradiated in a viscometer at room temperatures, polymerisation proceeds rapidly for some time after the light has been cut off. (This is independent of the normal photochemical after-effect.) On heating to 100° C. for a few minutes and cooling, the polymerisation is arrested. This may be due to destruction of catalyst or formation of inhibitor. Compelling evidence for the latter seems to be the observation that if after irradiation the vapour alone is heated, the reaction is also arrested. Eventually, after an induction period, it proceeds again. It is difficult to find any alternative interpretation of this effect.

The formation of inhibitor on heating has bearing on a recent paper by Dr. Walling. Walling finds that the initiation reaction in the thermal polymerisation of methyl methacrylate at temperatures in the neighbourhood of 100° C. has a very low frequency factor, ~ 1. It seems likely that this may be attributed to the formation of inhibitor in his experiments.

Finally the photopolymerisation gives some information as to the activity of the allyl radical. It has been stated that this radical is very inactive, and cannot enter into propagation reactions with monomers. Our experiments seem to show that it reacts readily with methyl methacrylate. A substituted allyl radical is presumably formed by chain transfer with methyl methacrylate. If this did not react it is unlikely

that our results would conform as well as they do to the kinetic equations, which are worked out on the assumption that all the transfer radicals react. Reference to Fig. 1 of our paper shows that the calculated and observed rates agree satisfactorily for light intensities varying by a factor of 10^5.

Dr. C. H. Bamford (*Maidenhead*) (*communicated*): The method of Bamford and Dewar may be used to investigate copolymerisation. Determination of $d\eta/dt$ over a range of light intensities, for different proportions of the two monomers A, B, together with analysis of the copolymers, will give the following information for two monomers of which the individual constants are known:

(1) the rate of "crossed" thermal initiation, $k'_1(A)(B)$;
(2) the crossed termination constant;
(3) the *total* chain transfer per kinetic chain;
(4) the value of the Staudinger constant as a function of the composition of the copolymer.

The production of initial centres in the thermal reaction has received comparatively little study, and (1) above should provide interesting results especially with pairs of monomers having different donor-acceptor properties.

Since in addition the crossed propagation constants are known directly from the copolymer compositions and the individual propagation constants, it will be clear that 12 of the 14 velocity constants may be determined absolutely. The remaining two (transfer) constants are not separable, but a relation between them is obtained which determines (3) above.

Mr. G. Dixon-Lewis (*Maidenhead*) said: I should like to take this opportunity of communicating the results of some preliminary determinations I have recently carried out of the velocity constants in the polymerisation of vinyl acetate at 0° C., using the method of Bamford and Dewar (p. 310). The values obtained for the constants are:

k_2 (propagation) = 1800
k_3 (transfer) = 0·123
k_4 (termination) = 2×10^8.

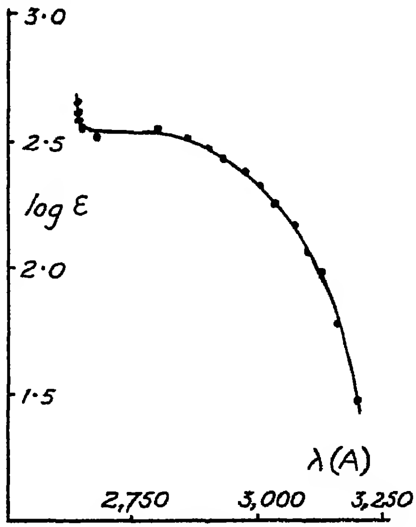

FIG. 1.

The rate in the absence of ultra-violet light is indistinguishable from zero, and k_1 (spontaneous initiation) is zero or very small.

It is interesting to compare these results for k_2 and k_4 with those recently published by Bartlett,[1] and by Burnett and Melville,[2] who both used sector methods for determining the mean life-time of the active particles.

	Bartlett (25° C.).	*B. and M.* (15·9° C.).	*Ours* (0° C.).
k_2	1,100	700	1,800
k_4	8×10^7	3×10^9	2×10^8

[1] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 2377; Swain and Bratlett, *ibid.*, 1946, 68, 2381.
[2] Burnett and Melville, *Proc. Roy. Soc. A*, 1947, **189**, 456

The present results agree satisfactorily with those of Swain and Bartlett, but Melville's value for the termination is much higher. This may be due to two causes.

(*a*) The chief reason is probably that mentioned by Swain and Bartlett that the light used by Melville (who employed a 50% acetic acid filter), is half absorbed by pure vinyl acetate in a distance of 2·3 mm. or less, whereas the length of his cell was 4·0 cm. This means that all the active particles are concentrated in a small portion of the reaction cell. Further, Melville's light absorption by the monomer is much higher than that recently measured by us on the fractionated product (Fig. 1). It is possible that his product contains small amounts of acetaldehyde or other impurities.

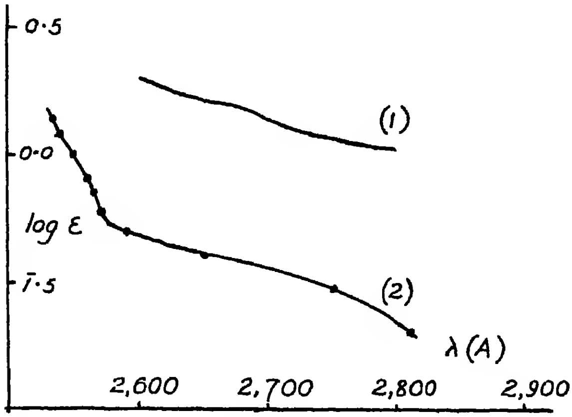

FIG. 2.

It might be mentioned that in the present work it was necessary to use a hot 50 % acetic acid filter to produce a high enough light intensity for the application of the method with the mercury arc employed. Such a filter lets through 2650 A. and a very small amount of light of shorter wave-length down to 2550 A. This might explain the fact that our value for k_4 is slightly higher than Bartlett's.

(*b*) In view of the absorption spectrum we have just measured for quinone (Fig. 2, which also agrees with the published one by Klingstedt [8]), it would seem that this substance may exert an internal filter effect at the wavelengths used by Melville, e.g. at 2900 A., ϵ is about 300, and a concentration of about 0·004 M. or 4 mg. in 10 cc. can absorb as strongly in this region as the 10 M. vinyl acetate. Therefore, unless light absorbed by quinone acts with a quantum efficiency of unity and prevents it from acting as an inhibitor, the inhibitor method of counting the rate of chain starting is open to question.

Dr. M. J. S. Dewar (*Maidenhead*) (*communicated*) : During this Discussion the problem of radical termination has been raised several times. I should like to point out that the work of Bamford and Dewar reported here (p. 310) shows quite unambiguously that in the polymerisations of styrene and of methyl methacrylate, termination occurs by disproportionation and not by combination. It is easily shown that in these reactions, where double-headed radicals are involved, the molecular weight of the polymer would be virtually independent of the rate of initiation if termination took place by combination of radicals; our results show that the molecular weight varies greatly with the rate of initiation, and in the manner calculated for disproportionation.

This result throws some doubt on the conclusions of Prof. Evans and his collaborators, who found that methyl polymethacrylate, prepared by the action of OH radicals, contains two OH groups per molecule of polymer. Possibly termination in their system involved combination of hydroxyl and polymer radicals.

These points will be discussed in more detail elsewhere.

Dr. J. Weiss (*Newcastle*) said: The question of the magnetic pro-

[8] Klingstedt, *Compt. rend.*, 1923, 176, 1550.

perties of certain organic molecular compounds has been raised. If the two component molecules are originally in a diamagnetic state then the electron transfer should result in the formation of "odd" ions, each with a spin magnetic moment ($s = \frac{1}{2}$) if one assumes only a loose coupling between the electrons and the rest of the molecule. It is found, however, that most of the molecular compounds in the *solid* state are diamagnetic. If, on the other hand, one can get them into solution one observes paramagnetism as, for instance, the alkaline solutions of the duroquinone quinhydrones are paramagnetic (Michaelis). It is thus most likely that in the solid state the lowest state corresponds to a quenching of the spins i.e. the paramagnetism is quenched by "exchange demagnetisation". To settle this point one would have to show, however, that the exchange integral is negative in this particular case. Although a detailed calculation is very difficult to carry out, it is, however, conceivable that this might be the case as one can replace the system (*a*) by the system (*b*),

$$(a)\quad \underset{+}{\bullet}\!\!-\!\!-\!\!-\!\!-\!\!\underset{-}{\bullet} \qquad\qquad (b)\quad \overset{1-}{\underset{2+}{\bullet}}\!\!-\!\!-\!\!-\!\!-\!\!\overset{1-}{\underset{0}{\bullet}}$$

which latter represents closed shells with two electrons outside which would lead to an exchange integral of the H_2-molecule type. This makes it very likely that the lowest state is the one with quenched spins. In the crystals one also has a high "magnetic concentration" which favours "exchange demagnetisation", while in solution—e.g. alkaline solutions of quinhydrones where the dimerisation is suppressed—one should expect paramagnetism, which is in agreement with the experimental observations.

Prof. M. G. Evans (*Leeds*) said: The experimental results and the theoretical discussion presented in this section seem to illustrate in broad outline the general principles enunciated in the introductory paper, namely, that there are three effects operating in determining the activation energy of reactions between radicals and monomers. These are (i) the heat of reaction, which can be related to the resonance energies of the radicals and the monomer, (ii) the character of the repulsion energy between the radical and the monomer and (iii) the resonance energy of the transition state. The details of this broad scheme have now to be filled in by determining activation energies for the radical reactions and the dissociation energies of the particular bonds involved. Dr. Dewar has referred to calculations he has made on the influence of substituents on the resonance energy in the initial and in the transition state using the method developed by Pauling and Wheland in which a substituent was assumed to have an effect on the electron affinity of the carbon centre to which it was attached; we [4] have carried out similar calculations for polymerisation steps. I feel, however, that the most important feature of such a treatment is the influence of the substituent on the electron distribution and hence on the coulombic interaction between the reaction centres. Our experience is that in many cases this term is much more important than the influence of the substituent on the resonance energy. In saying this, one is not denying the influence of substituents on the resonance energy in the transition state, but in this connection I think it is important to notice that in the work reported by Mayo and Walling it seems to be in those cases where ionic forms of the transition state have a low energy or are relatively stable, that major effects are introduced.

[4] See Seaman, *Thesis* (Leeds University); Evans, Gergeley and Seaman (in press).

B.—CHAIN TRANSFER AND INHIBITION.

THE DETERMINATION OF TRANSFER COEFFICIENTS IN POLYMERISATION REACTIONS.

By G. M. Burnett and H. W. Melville.

Received 26th June, 1947.

Since ethylenic polymerisation reactions are predominantly free radical in character the presence of solvent will, in most cases, modify considerably the course of the polymerisation. Chain transfer, whereby a reaction between the growing polymer radical and a solvent molecule results in the production of an inactive polymer molecule and a new radical from the solvent residue, was first suggested by Flory,[1] but little use has been made of this concept in the study of polymerisation reactions in solution. The systematic investigation of the kinetics of this type of reaction appears to present a convenient method of gaining a great deal of information on the nature and reactivity of free radicals and is also closely bound up with the problem of copolymerisation and the action of retarders.

Mayo [2] derived an expression, from which one may, having determined the mean degree of polymerisation, obtain the value of the *ratio* of the transfer to the propagation coefficients, but the expression is limited in its applicability to those reactions in which the rate of initiation is proportional to the square of the monomer concentration. This relationship does hold in the case of the thermal polymerisation of styrene and, from data on the degrees of polymerisation of styrene prepared in different solvents, much information on transfer reactions was obtained. There was, however, little investigation of the dependence of the rate of polymerisation on the concentration of the monomer which, as it turns out, is an important criterion of the nature of the intermediate free radical.

The radical formed as a result of the transfer reaction may fall into one of four distinct classes, although there is the possibility that there may be some overlapping of these classes.

(1) The radical may be relatively unstable and, therefore, of considerable reactivity so that it reacts quickly with the monomer to initiate a new chain of polymerisation. Thus the time between the stopping of one chain and the starting of the next is very small and the rate of reaction is not relatively reduced by the presence of the solvent. This may also be argued from the fact that the solvent, by taking part in the reaction, prevents the normal chain-terminating mechanism from operating.

(2) If the radical formed is very stable then it may add on to the monomer only very slowly so that there is an appreciable time lag in the overall propagation of chains. This time lag will depend primarily on the degree of stability of the free radical and on the inherent reactivity of the monomer and, as a result, the overall rate of polymerisation will be relatively reduced.

(3) The radical may be incapable of the initiation of fresh chains and is eventually removed by reaction with another of its kind.

(4) In this case the radical is again incapable of the initiation of new chains but is removed by interaction with another growing radical. These two classes fall into the general theory of retarders and are, therefore, of little interest here.

[1] Flory, *J. Amer. Chem. Soc.*, 1937, 59, 241. [2] Mayo, *ibid.*, 1943, 65, 2324.

It should be noted that the kinetic chain length in the case of a pure transfer reaction, is unaffected by the presence of the solvent although the degree of polymerisation will fall since each kinetic chain will be represented in the heterodisperse polymer as a number of polymer molecules each forming a part of the kinetic chain. The number of breaks in the kinetic chain must obviously depend on the absolute rate of the transfer and propagation reactions.

Since the individual values of the initiation, propagation and termination coefficients have been determined for vinyl acetate it now becomes practicable to investigate transfer with this molecule. Further, as will be shown below, the absolute value of the transfer coefficients can be determined and a method is suggested for determining the absolute values of the coefficients for the reaction of the radicals produced from the solvent molecules with the monomer when these coefficients are smaller than a certain value.

Kinetic Analysis.

It is possible to investigate fairly fully the kinetics of this type of reaction from a theoretical standpoint. The assumption is made that the velocity of any reaction involving the monomer or solvent molecules is proportional directly to their concentrations. Experiments with ethyl acetate solutions quantitatively confirm this (see Table I). The following reactions are considered as representing those which may occur in a system polymerising in solution; the symbols employed have the following meaning: P_n denotes an active polymer molecule of n monomeric units and M_n is the corresponding dead polymer, whether it be produced by the normal termination mechanism or by some transfer reaction, AS is a molecule of solvent and S— is the free radical from the solvent.

(*a*) Initiation.	$M = P_1$	I
(*b*) Propagation.	$M + P_n = P_{n+1}$	k_{p_n}
(*c*) Transfer to monomer.	$M + P_n = M_n + P_1$	k_{r_n}
(*d*) Transfer to solvent.	$P_n + AS = M_n + S^-$	k_{f_n}
(*e*) Restarting of chains.	$M + S— = P_1$	k_s
(*f*) Termination.	$P_m + P_n = M_{m+n}$	k_{m_m}, k_{m_n}
(*g*) Removals of free radicals.	$2S— = ?$	k_e

There is also the possibility of the reaction

$$P_n + S— = M_n$$

which will be ignored here since it falls into the category of an inhibition reaction.

CASE I. If transfer alone occurs and a stationary state has been established we will have

$$d(P_1)/dt = I + k_s(S—)(M) + (M)\sum k_{r_s}(P_s) - k_{p_1}(P_1)(M) - k_{r_1}(P_1)(M) - k_{f_1}(P_1)(AS) - k_{m_1}(P_1)\sum k_{m_s}(P_s) = 0$$

and generally,

$$d(P_n)/dt = k_{p_{n-1}}(P_{n-1})(M) - k_{p_n}(P_n)(M) - k_{r_n}(P_n)(M) - k_{f_n}(P_n)(AS) - k_{m_n}(P_n)\sum k_{m_s}(P_s) = 0.$$

The addition of these equations to infinity leads to

$$I + k_s(M)(S—) - (AS)\sum k_{f_s}(P_s) - \left\{\sum k_{m_s}(P_s)\right\}^2 = 0. \quad (1)$$

Also, if a stationary state exists, then

$$d(S—)/dt = (AS)\sum k_{f_s}(P_s) - k_s(S—)(M) - k_e(S—)^2 = 0.$$

In the first place we shall consider that the last term of this equation is insignificant, i.e., all the S— radicals are used in the starting of fresh chains, so that,

$$(\mathrm{AS}) \sum k_{f_s}(\mathrm{P}_s) - k_s(\mathrm{S}—)(\mathrm{M}) = 0$$

and so

$$I^{\frac{1}{2}} = \sum k_{m_s}(\mathrm{P}_s).$$

The overall rate will be given by

$$-\,\mathrm{d}(\mathrm{M})/\mathrm{d}t = (\mathrm{M}) \sum k_{p_s}(\mathrm{P}_s) + k_s(\mathrm{M})(\mathrm{S}—) + (\mathrm{M}) \sum k_{r_s}(\mathrm{P}_s)$$
$$= (\mathrm{M})\left\{\sum k_{p_s}(\mathrm{P}_s) + \sum k_{r_s}(\mathrm{P}_s)\right\} + \sum k_{f_s}(\mathrm{P}_s)(\mathrm{AS}).$$

Now, since it has been shown that, at least for long chains,

$$k_{m_s} = \delta^{-1}k_{p_s} = \gamma^{-1}k_{r_s} = \phi^{-1}k_{r_s}$$

are relationships which are independent of molecular size, we have

$$-\,\mathrm{d}(\mathrm{M})/\mathrm{d}t = (\mathrm{M})I^{\frac{1}{2}}\{\delta + \gamma + \phi(\mathrm{AS})/(\mathrm{M})\}.$$

Case II. If the free radicals are incapable of initiating new chains then it is evident that in the extreme case in which all the chains are stopped by a transfer mechanism

$$\mathrm{d}(\mathrm{P}_1)/\mathrm{d}t = I + (\mathrm{M}) \sum k_{r_1}(\mathrm{P}_s) - k_{p_1}(\mathrm{P}_1)(\mathrm{M}) - k_{r_1}(\mathrm{P}_1)(\mathrm{M}) - k_{f_1}(\mathrm{P}_1\ (\mathrm{AS}) = 0$$

and

$$\mathrm{d}(\mathrm{P}_n)/\mathrm{d}t = k_{p_{n-1}}(\mathrm{P}_{n-1})(\mathrm{M}) - k_{p_n}(\mathrm{P}_n)(\mathrm{M}) - k_{r_n}(\mathrm{P}_n)(\mathrm{M}) - k_{f_n}(\mathrm{P}_n)(\mathrm{AS}) = 0.$$

Adding these equations, as before,

$$I/(\mathrm{AS}) = \sum k_{f_s}(\mathrm{P}_s)$$

and from this the rate of polymerisation can be shown to be

$$-\,\mathrm{d}(\mathrm{M})/\mathrm{d}t = (\mathrm{M})/(\mathrm{AS})\ \ (I/\phi)(\delta + \gamma).$$

Case III. In this case there is a partial loss of the intermediate free radicals by combination with their own kind. The stationary state equations will be as for case I but, in this instance, the equation governing the concentration of the intermediate free radicals will be a quadratic whose solution is

$$(\mathrm{S}—) = -k_s(\mathrm{M})\left\{1 - \left[1 + 4k_s(\mathrm{AS}) \sum k_{f_s}(\mathrm{P}_s)/k_s^{2}(\mathrm{M})^{2}\right]^{\frac{1}{2}}\right\}$$

If, as may occur under certain conditions, the second term under the square root is less than unity a binomial expansion is possible to give

$$(\mathrm{S}—) = \frac{(\mathrm{AS}) \sum k_{f_s}(\mathrm{P}_s)}{k_s(\mathrm{M})} - \frac{k_s(\mathrm{AS})^2 \left\{\sum k_{f_s}(\mathrm{P}_s)\right\}^2}{k_s^{3}(\mathrm{M})^{3}}.$$

Substituting this value for (S—) in equation (1) we have

$$I - \frac{k_s(\mathrm{AS})^2 \left\{\sum k_{f_s}(\mathrm{P}_s)\right\}^2}{k_s^{2}(\mathrm{M})^{2}} - \left\{\sum k_{m_s}(\mathrm{P}_s)\right\}^2 = 0.$$

This expression leads eventually to

$$-\,\mathrm{d}(\mathrm{M})/\mathrm{d}t = \frac{k_s(\mathrm{M})I^{\frac{1}{2}}}{k_s^{\frac{1}{2}}}\left\{\frac{\delta + \gamma}{\phi}(\mathrm{M})/(\mathrm{AS}) + 1\right\} - I.$$

It is evident from the results that in Case I the overall rate is proportional to the square root of the starting rate, in Case II, to the first power, and in Case III, to some power, n, where $\frac{1}{2} < n < 1$.

Experimental Results.

In the case of straightforward transfer reactions it has been shown that the rate of polymerisation is given by

$$R = (M)I^{\frac{1}{2}}\{\delta + \gamma + \phi(AS)/(M)\}.$$

Now,
$$I = k_i(R\ )(M)$$

where (R) is the concentration of the free radicals derived from the catalyst Hence if the catalyst concentration is kept constant at a given temperature

$$I = K^2(M)$$

so that
$$R = K(M)^{3/2}(\delta + \gamma + \phi\,(AS)/(M)).$$

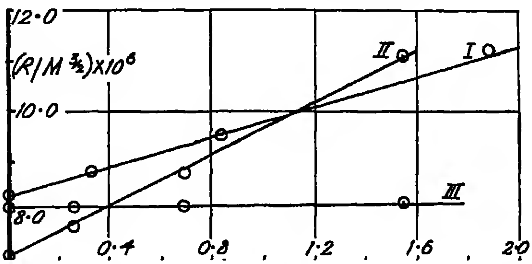

FIG. 1 —$R/M^{3/2}$ as a function of (AS)/(M) for normal transfer solvents
I Chloroform, II Carbon tetrachloride; III Ethyl acetate

Hence $R/M^{3/2}$ plotted as a function of (AS)/(M) will give a straight line whose intercept will be $K(\delta + \gamma)$ and whose slope is $K\phi$ In the case of the bulk polymerisation of vinyl acetate it has been shown that there is no detectable transfer

TABLE I —TRANSFER COEFFICIENTS IN VARIOUS SOLVENTS.

(AS)/(M).	Rate mol./l./sec.	$R/M^{3/2}$.	k_f l/mol/sec.
	Chloroform.		
0·000	$2·58 \times 10^{-4}$	$8\ 33 \times 10^{-6}$	—
0·314	$1·95 \times 10^{-4}$	$8·78 \times 10^{-6}$	195
0·837	$1·39 \times 10^{-1}$	$9\ 50 \times 10^{-6}$	220
1·884	$9\ 30 \times 10^{-5}$	$1·13 \times 10^{-5}$	216
			(207)
	Carbon Tetrachloride.		
0·000	$2·24 \times 10^{-4}$	$7·12 \times 10^{-6}$	—
0·257	$1·72 \times 10^{-4}$	$7·70 \times 10^{-6}$	407
0·686	$1·22 \times 10^{-4}$	$8\ 76 \times 10^{-6}$	425
1·545	$8·90 \times 10^{-5}$	$1·11 \times 10^{-5}$	440
			(430)
	Ethyl Acetate.		
0·000	$2·56 \times 10^{-4}$	$8·09 \times 10^{-6}$	—
0·258	$1·90 \times 10^{-4}$	$8·07 \times 10^{-6}$	—
0·688	$1·33 \times 10^{-4}$	$8·17 \times 10^{-6}$	—
1·548	$0·66 \times 10^{-4}$	$8·19 \times 10^{-6}$	—
			(<0·5)

so that it may be assumed that $\delta \gg \gamma$ When (AS)/(M) is zero we will have the value of K, since we know the experimental value of δ at 54·6° C. is $2·7 \times 10^{-3}$. Hence ϕ and, therefore, k_f become measurable

Fig. 1 shows $R/M^{3/2}$ plotted against (AS)/(M) for the peroxide-catalysed polymerisation of vinyl acetate in ethyl acetate, chloroform and carbon tetrachloride at 54·6° C. Using the methods of calculation of k_f set out above the results shown in Table I may be found. In this table the individual values for k_f in the case of ethyl acetate solutions are not given since the overall change in the values of the third column lie well within the expected experimental error so that very small deviations will be too greatly magnified for the results to have any significance. In Table I also the mean value of k_f, obtained from the slopes of the graphs of Fig. 1 are given in brackets.

From these results it is evident that the free radical derived from carbon tetrachloride, CCl_3—, is capable of initiating chains although Mayo [8] has doubted that this is possible. If no chain initiation had occurred then it is evident that the linear dependence of $R/M^{3/2}$ would not have held. This dependence simultaneously proves the existence of transfer and also that the rate of polymerisation is proportional to the square root of the catalyst concentration.

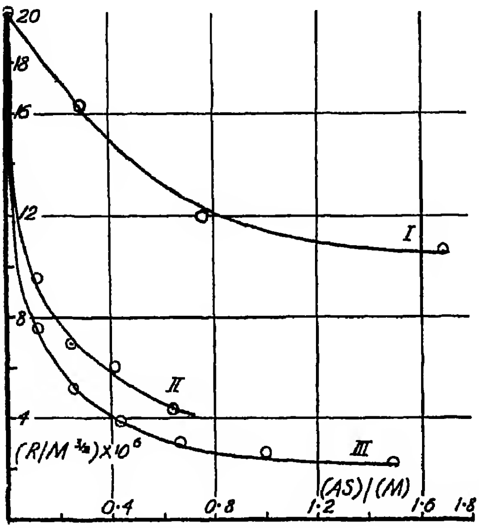

FIG. 2.—$R/M^{3/2}$ as a function of (AS)/(M) for aromatic solvents. I Benzene; II Toluene; III Chlorobenzene.

Each of the solvents which have been described would give rise to intermediate free radicals which would be expected to be comparatively active, so a series of solvents was examined whose residues would give relatively stable radicals. The solvents used were benzene, toluene and chlorobenzene whose action is evidently different from that just described, as will be seen from Fig. 2.

From this there must be either an inhibitory action by the solvent due to the fact that the intermediate radicals fall into class (3) or (4) or that the time-lag between the cessation of one chain and the initiation of the next has become appreciable owing to the inability of the solvent radical to propagate chains rapidly, i.e. class (2). To test this point some experiments were carried with toluene solutions to find the dependence of the rate of polymerisation on catalyst concentration. The results of these experiments are shown in Table II.

TABLE II.—EFFECT OF CATALYST CONCENTRATION ON RATE IN TOLUENE SOLUTION.

Catalyst Conc. mol./l. × 10^3.	Rate mol./l./sec. × 10^5.	$R/C^{\frac{1}{2}}$ × 10^4.	R/C × 10^3.
80 % monomer by volume in toluene.			
6·25	6·60	8·32	10·50
12·50	9·21	8·51	7·39
15·60	10·80	8·67	6·94
25·20	15·30	9·66	6·08
50·40	20·30	9·08	4·04
40 % monomer by volume in toluene.			
25·20	2·64	1·67	10·51
50·40	3·90	1·75	7·74
75·60	4·58	1·65	6·04
100·80	5·31	1·67	4·94

In neither case are the values in the third column much removed from constancy so that it may be deduced that the rate of polymerisation is proportional to the square root of the catalyst concentration, which means that the final stopping of the chains is by the normal mutual destruction of two of the growing chains. It is evident from the curves of Fig. 2 that the same method of calcula-

tion of k_f cannot be used in this case as for the straight-chain compounds. The calculation can, however, be effected in the following manner.

If P is the degree of polymerisation of the polymer produced in the solution and P_0 of the polymer formed in bulk with the same catalyst concentration and temperature, it is easy to show that, providing the conversion is not great,

$$1/P = (M_0)^{\frac{1}{2}}/(M)^{\frac{1}{2}}(1/P_0) + (k_f/k_p)(AS)/(M)$$

TABLE III.

Monomer.	(AS)/(M).	Mol. Wt.	$(1/P) \times 10^4$.	k_f.
10·0	0	240,000	3·91	—
8·0	0·281	180,000	4·78	0·42
6·0	0·750	110,000	6·89	0·38
4·0	1·685	85,000	10·20	0·41

Hence the mean value of k_f is 0·40 ± 0·02. l./mol./sec.

where (M) and (M_0) are the concentrations of the monomer in solution and in bulk respectively. The molecular weight of the polymer produced was measured osmometrically and the following results were found for benzene.

Discussion.

The foregoing results indicate that the nature of the free radical formed by the transfer to the solvent plays an important part in the course of the reaction. So far, however, we have been unable to assess quantitatively the effect of the radical which involves the determination of the fundamental quantity, k_s, the velocity coefficient for the addition of the radical to the monomer. If k_s is low then we should expect that this step would become a rate-controlling stage in the reaction, which has been shown to be true in the case of the aromatic solvents. Qualitatively the description of the phenomenon is not difficult.

The ultimate determination of the value of k_s appears to lie in the use of a sector technique with the added consideration that a photosensitiser may be required to start the chains in order to overcome the possibility of internal filtering. The investigation of photosensitisers does not appear to be far enough advanced to make their use generally applicable. If a sector method was used then the lifetime of the kinetic chain would be determined, i.e. the time from the initiation to the eventual termination of the chains by mutual destruction of two of the growing radicals. If the lifetime of the chains in bulk is known then the lifetime in solution may be calculated on the assumption that the solvent acts merely as a diluent. The difference between this calculated value and the measured one will give the total time-lag due to transfer and from a knowledge of the average number of breaks per chain the lag per break can be found and hence k_s can be calculated. It is obvious that the determination of k_s for a number of solvents using the same polymerisation system, would lead to a method of determining the relative activities of the free radicals involved, but it is unlikely that the present technique will be able to cope with cases in which the value of k_s is high.

We wish to thank the Department of Scientific and Industrial Research for granting a senior award to one of us (G. M. B.).

Summary.

The polymerisation of vinyl acetate in a number of solvents has been studied with a view to determining the absolute values of the reaction velocity coefficients for the transfer reaction. Two methods of calculation are described, the method applicable depending on the solvent used. The reason for the difference in behaviour appears to be that in the case of the short-chain compounds the radicals produced by transfer are highly reactive, whereas in the case of aromatics the radicals are relatively inactive so that there is a lag in the propagation of the polymerisation chains. This is somewhat like the action of a retarder but the overall rate of polymerisation is proportional to the square root of the concentration of the catalyst, so that the termination of the kinetic chains must occur by mutual termination.

Résumé.

La polymérisation de l'acétate de vinyle a été étudiée dans un certain nombre de solvants en vue de déterminer les valeurs absolues des coefficients de vitesse pour la réaction de transport, on décrit deux méthodes de calcul, qui dépendent du solvant employé—les différences de comportement peuvent être expliquées si l'on suppose que les radicaux produits par transport sont hautement réactifs dans le cas des composés à chaînes courtes, tandis qu'ils sont relativement inactifs dans le cas des composés aromatiques, de telle sorte qu'il y a retard dans la propagation de la chaîne de polymérisation.

Zusammenfassung.

Die Polymerisation von Vinylacetat wurde in einer Reihe von Lösungsmitteln untersucht, um die absoluten Werte der Geschwindigkeitskoeffizienten fur die Übertragungsreaktion festzustellen. Zwei Berechnungsmethoden—je nach der Art von Lösungmittel—werden beschrieben. Das verschiedenartige Verhalten wird dadurch erklärt, dass angenommen wird, dass die durch Übertragung erzeugten Radikale im Falle von kurzen Kettenverbindungen hochreaktiv sind, aber dagegen für aromatische Verbindungen verhältnismässig unreaktiv sind, sodass id diesem Fall eine Verzögerung in der Fortpflanzung der Polymerisationsketten eintritt.

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CHAIN TRANSFER IN THE POLYMERISATION OF STYRENE III. THE REACTIVITIES OF HYDROCARBONS TOWARD THE STYRENE RADICAL.

By R. A. Gregg and Frank R. Mayo.

Received 6th August, 1947.

The object of the present work is to compare the relative reactivities of twelve hydrocarbons toward the substituted benzyl radical in polymerising styrene and to discuss the effect of hydrocarbon substituents on the ability of a carbon-hydrogen bond to undergo chain transfer with this radical. Assuming a simple competition between monomer and solvent for the polymer radical, an earlier paper [1] correlated the reactivity of a solvent with the molecular weight of the resultant polymer in uncatalysed polymerisations by the equation

$$1/\bar{P} = C[\mathrm{SX}]/[\mathrm{M}] + 1/P_0 \quad . \quad . \quad . \quad . \quad (1)$$

where $\bar{P}$ is the average degree of polymerisation attained at solvent and monomer concentrations, [SX] and [M], where $\bar{P}_0$ is the degree of polymerisation in the absence of solvent, and where C is the transfer constant, dependent on the solvent, monomer, and temperature used. Since the transfer constant is the ratio of the rate constants for chain transfer and chain growth for the radical considered, the relative reactivities of solvents toward that radical are in the same ratios as their transfer constants. After application of the equation to limited published data had given encouraging results,[1, 2] the relations were given a thorough test in the

[1] Mayo, *J. Amer. Chem. Soc.*, 1943, **65**, 2324.
[2] Similar developments were published almost simultaneously by Hulbert, Harman, Tobolsky and Eyring, *Ann. N.Y. Acad. Sci.*, 1943, **44**, 371; and by Medvedev, Koritskaya and Alekseeva, *J. Physic. Chem. U.S.S.R.*, 1943, **17**, 391.

polymerisation of styrene in CCl_4.[3] These experiments agreed with eqn. (1) within experimental error over solvent/monomer ratios from 0-2 and average degrees of polymerisation from about 9000 to 50. Similar equations [3] and principles apply to peroxide-catalysed polymerisations.*

Experimental.

Materials.—Styrene was prepared for use as described elsewhere.[3] The purest commercially obtainable hydrocarbons (if liquids) were freed of peroxides by refluxing with sodium; they were then distilled from sodium or potassium through a l-m. helices-packed column in an all-glass still under an atmosphere of nitrogen. The total boiling-point range of the fractions used is given below; thermometer readings are usually uncorrected. Refractive indices, n_D^{20}, as listed by the National Bureau of Standards,[4] are included in parentheses for reference.

Benzene: 78·8-79·0° at 1 atmos., n_D^{20} 1·5009 for 60° experiments; 80·0° at 764 mm., n_D^{20} 1·5012 for 100° experiments; and, 79·2° at 762 mm., n_D^{20} 1·5017 for 132° experiments (1·50110).

tert-Butylbenzene: 167·7-168·0 at 764 mm., n_D^{20} 1·4965.

Toluene: 110·0° at 758 mm., n_D^{20} 1·4957 (1·49682).

Ethylbenzene: 132·0-132·2° at 750 mm., n_D^{20} 1·4957-1·4959 for 60° experiments; 134·6° at 758 mm., n_D^{20} 1·4959 for 100° and 132° experiments (1·49580).

iso-Propylbenzene: 151·4-151·9 at 1 atmos., n_D^{20} 1·4910-1·4912 (1·49125).

Cyclohexane: 79·8° at 765 mm., n_D^{20} 1·4262 (1·42623).

n-Heptane: 97·0° at 764 mm., n_D^{20} 1·3876 (1·38764).

Tetralin: 92·7° at 19·5 mm., n_D^{20} 1·5410.

Immediately before use these liquids were redistilled from sodium or potassium under nitrogen using a Vigreux column. The solids were repeatedly crystallised until they possessed a sharp melting point.

Procedure.—The procedure followed that described elsewhere.[3] Weighed quantities of styrene and the hydrocarbon in glass ampoules were thoroughly degassed and sealed under high vacuum. No catalyst was employed. After the reaction period, the polymers were precipitated with methanol and dried. From the intrinsic viscosities in benzene at 30°, the degrees of polymerisation were calculated by use of the relation,† [3]

$$\overline{M}_n = 184{,}000\,[\eta]^{1\cdot 377} = 104P \qquad (2)$$

Degrees of polymerisation were taken as (number average molecular weight)/104, corrections for end groups being negligible in the present paper.

Results and Discussion.

Experimental results are collected in Table 1 and in some cases the transfer constants were determined graphically from Fig. 1-3. The best values of the transfer constants are then summarised in Table II. The conversions of monomer to polymer were small enough to permit use of the differential eqn. (1). The overall second-order rate constants,‡ (k_2), show that the rate constants for chain initiation and termination (in $1/\overline{P}_0)^1$ and for chain growth are substantially

[3] Gregg and Mayo, paper submitted to *J. Amer. Chem. Soc.*

* Eqn. (1) does not apply to low degrees of polymerisation because its development neglected consumption of monomer by solvent radical (k[S·][M], equal to k_4[R·][SX])[1]. When this addition is made, and all chains are assumed to end by transfer, then $\overline{P} = ([M]/C[SX]) + 1$. Study of very low molecular weight products from styrene and carbon tetrachloride has shown that the shortest radicals have abnormally low transfer constants. Neither of these considerations applies in the present paper.

[4] Forziati, Glasgow, Wellingham and Rossini, *Bur. Stand. J. Res.*, 1946, **36**, 129.

† We are indebted to Dr. R. H. Ewart, H. C. Tingey and M. Wales of these Laboratories for establishment of this relation.

‡ Volumes were calculated from weights of reagents and literature values of densities at 20°.

independent of the solvent and length of the radical. Occasional experiments showed very large rate constants and were rejected as containing accidental impurities. *n*-Heptane, which precipitated polystyrene as it formed, gave lower rate constants at higher solvent concentrations. While these observations throw some doubt on the applicability of the method in this solvent, the transfer constant is nevertheless independent of solvent-monomer ratio. The somewhat higher rate of polymerisation in diphenylmethane may be due to a retained trace of peroxide and may result in a somewhat high value of the transfer constant. However, in general, the transfer constants are highly reproducible and are probably accurate within the errors listed in Table I.

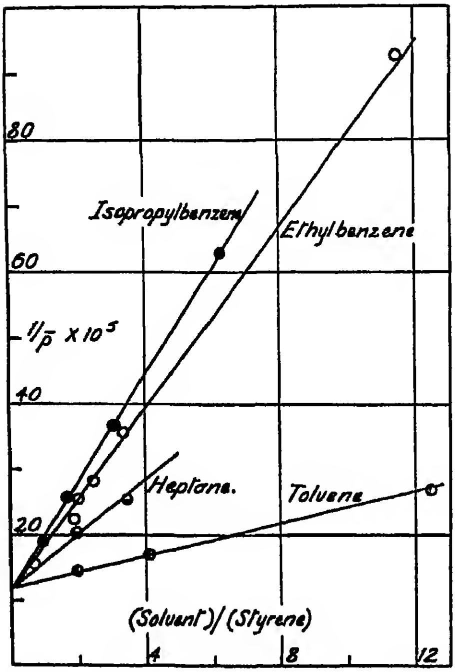

FIG. 1.—Polymerisations of styrene in hydrocarbons at 60°.

Although the present results support qualitatively and extend the results of the first paper,[1] there are significant quantitative differences. The accuracy of the transfer-constant determinations is dependent upon the accuracy of the experimentally-determined number-average molecular weights. Having directly related intrinsic viscosities to number-average molecular weights through osmotic molecular weight determinations and end-group analyses on whole polymers, our number-average molecular weight determinations should be more reliable than those of Schulz and of Suess and collaborators,[5] based on the Staudinger equation and relating constants for homogeneous and whole polymers by a theoretical relation not applicable when chains end by transfer. All of our degrees of polymerisation are larger than theirs for corresponding experiments, our values for polystyrene prepared in absence of solvent at 100° and 132° being 3770 and 1760 as compared with 2160 and 1490 for Schulz and 1900 at 100° for Suess. The result is that the new transfer constants for benzene and cyclohexane are smaller at 100°, leading to larger experimental activation energies and larger differences between solvents.

The results will now be discussed on the basis that the transfer constant of each hydrocarbon is directly proportional to the sum of the absolute rate constants for the reaction of each hydrogen atom in the solvent with a styrene-type radical. Benzene and cyclohexane are the least reactive solvents: they have so little effect in reducing the molecular weight of styrene, especially at 60°, that their transfer constants are subject to the largest uncertainty. The higher value for heptane is of doubtful significance, as already noted, but the higher activity of *tert*-butylbenzene, in comparison with benzene, points to an effect of the 9 aliphatic hydrogen atoms in addition to that of the 5 aromatic hydrogen atoms. The transfer constant for decalin is also subject to more than the

[5] (*a*) Suess, Pilch and Rudorfer, *Z. physik. Chem. A*, 1937, 179, 361; (*b*) Suess and Springer, *ibid. A*, 1937, 181, 81; (*c*) Schulz, Dinglinger and Husemann, *ibid. B*, 1939, 43, 385.

usual uncertainty, although a greater activity than the other aliphatic hydrocarbons would be anticipated from the fact that it contains two tertiary hydrogen atoms.

The greater activity of toluene and ethylbenzene over benzene has previously been ascribed to the benzyl hydrogen atom and to the increasing effect of substitution on the α-carbon atom.[1] This conclusion is now supported by the still higher activity of *iso*propylbenzene, with a tertiary benzyl hydrogen atom, and the low activity of *tert*-butylbenzene, with no benzyl hydrogen atom. This conclusion is confirmed by the recent work of Kharasch, McBay and Urry [6] who have shown that the radicals from decomposing acetyl peroxide remove the α-hydrogen atoms from ethylbenzene and *iso*propylbenzene, leaving the substituted benzyl residues to dimerise. Diphenylmethane, triphenylmethane, and fluorene show an increasing activity in chain transfer which must be due to the decreasing strength of the methane carbon-hydrogen bond. The acidities of the hydrocarbons determined by Conant and Wheland [7] and by McEwen [8] are in the same order as the transfer constants. The identical orders are probably due to the same factors, increasing resonance stabilisation of the radical formed by loss of a hydrogen atom, or of the negative ion formed by the loss of a proton. However, this analogy between reactivity toward radicals and acidity is not applicable to many compounds where other than carbon-hydrogen bonds are attacked.

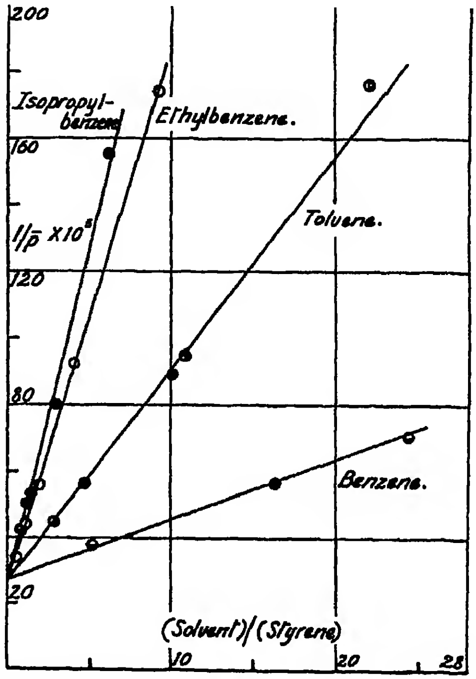

FIG. 2.—Polymerisations of styrene in hydrocarbons at 100°.

All of the above results point to the conclusion that the *benzyl* hydrogen atoms are the points of attack favoured by the radical derived from styrene. The products of direct bromination and of sulfuryl chloride chlorination of such hydrocarbons in the presence of light or peroxide catalysts point indisputably to the same conclusion,[9] although addition to the nucleus accompanies direct side-chain chlorination. On the other hand, diazotised *p*-toluidine and *p*-bromoaniline couple in the 2- and 4- positions of toluene to give the substituted 2- or 4-methylbiphenyls,[10] and the decompositions of *N*-nitrosoacetanilide [11] or of benzoyl peroxide [12]

[6] Kharasch, McBay and Urry, *J. Org. Chem.*, 1945, **10**, 401.
[7] Conant and Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1212.
[8] McEwen, *ibid.*, 1936, **58**, 1124.
[9] Kharasch *et al.*, *J. Org. Chem.*, 1938, **3**, 53; 1941, **6**, 810; *J. Amer. Chem. Soc.*, 1939, **61**, 2142; Sampey, Fawcett and Morehead, *ibid.*, 1940, **62**, 1839.
[10] Gomberg and Pernert, *ibid.*, 1926, **48**, 1372.
[11] Grieve and Hey, *J. Chem. Soc.*, 1934, 1797.
[12] Gelissen and Hermans, *Ber.*, 1925, **58**, 476.

in toluene give 2- and 4-methylbiphenyls. Aromatic radicals,[13] then, do not behave like benzyl radicals or bromine atoms toward alkylbenzenes.

The hydrocarbons thus far discussed range from a very low activity in chain transfer to an activity comparable to that of CCl_4, but even the latter is not very reactive in that the rate constant for chain transfer is only about 1 % as large as the rate constant for chain growth in the polymerisation of styrene. Pentaphenylethane, however, has a transfer constant of about 2, of the same order as the transfer constants of the mercaptans.[14] The results are complicated somewhat by the fact that the polymerisation proceeded at about twice the normal rate in this "solvent," a result which may be due to peroxidic impurities or to slight dissociation into radicals.[15] There is at present no indication as to whether the activity of this hydrocarbon lies in the ethyl-hydrogen or ethane carbon-carbon bond, or both.

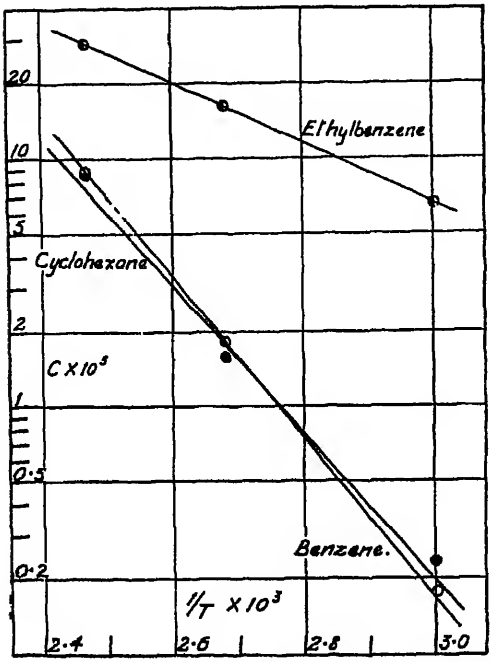

FIG. 3.—Temperature dependence of transfer constants.

We shall now consider the quantitative effects of substituents on the rates of reaction of carbon-hydrogen bonds using experimental activation energies and frequency factors listed in Table II. Arrangement of the hydrocarbons in order of increasing activity in chain transfer shows that the experimental activation energies for chain transfer decrease in the same order, with one exception. Thus, the least activation energy is required to form the most stable radical and resonance contributions to the activated state from the radical being formed are important in reducing the strength of the bond and the activation energy required for transfer of a hydrogen atom. A similar factor has been shown to be important in determining the rates of addition of free radicals to double bonds in copolymerisation.[16] However, Table II likewise shows the temperature-independent factor to be very important in free-radical transfer reactions. Thus, the ratio of transfer constants at 100° for *iso*-propylbenzene and benzene is only 10·9; the ratio would be 270,000 for a difference of 9·3 kcal./mole in activation energies if the frequency factors were constant. Table II shows the decrease in values of the frequency factor almost parallels the decrease in experimental activation energy for the reaction of radicals with hydrocarbons, and this dependence is shown graphically in Fig. 4 from which is derived the approximate mathematical relation :

$$(E_t - E_s) = 6{\cdot}5 + 0{\cdot}91 \ln (A_t / A_s). \qquad (3)$$

[13] Waters, *Chemistry of Free Radicals* (Oxford, 1946).
[14] Smith, *J. Amer. Chem. Soc.*, 1946, 68, 2059; Gregg, Alderman and Mayo (unpublished work).
[15] Bachman and Osborne, *J. Org. Chem.*, 1940, 5, 29.
[16] Mayo, Lewis, and Walling, this Discussion.

TABLE I.—THERMAL POLYMERISATION OF STYRENE IN HYDROCARBONS *in vacuo*.

Solvent / Styrene (moles).	Yield (%).	Time (hr.).	k_2^a (× 10^4).	$[\eta]^b$.	$1/\bar{P}$ (× 10^5).	C^c (× 10^5).
Experiments at 60°.						
0·00 (mean of several expts.)			1·1	3·43	11·7 ($1/P_0$)	
Solvent : Benzene.						
2·95	7·07	231·7	1·28	3·19	12·8	0·37
6·55	7·51	356·5	1·52	2·69	15·9	c·64
5·58	5·91	379	1·03	3·39	11·8	0 02
8·27	3·63	384	0·85	3·36	11·9	0·02
15·5	2·96	520	0·90	2·78	14·5	0·18
					best	0·18 ± 0·1
Solvent : Cyclohexane.						
4·43	6·05	376·6	1·06	3·18	12·7	0·23
14·7	3·54	640	1·00	2·80	15·2	0·24
5·00	5·91	242	1·71	3·02	13·7	0·40
					best	0·24 ± 0·1
Solvent : *tert*-Butylbenzene						
2·00	8·26	231·7	1·65	3·20	12·3	0·30
3·31	9·95	279·3	2·49	2·86	14·6	0·87
					best	0·6 ± 0·3
Solvent : Toluene						
1·97	7·50	231·8	1·15	2·90	14·5	1·4
4·11	7·12	279·4	1·50	2·55	17·0	1·3
12·43	5·05	476	1·62	1·78	26·9	1·2
					best	1·25 ± 0·2
Solvent : Ethylbenzene.						
0·70	6·97	136	1·12	2·75	15·5	5·4
1·88	6·05	192	1·16	2·13	22·2	5·6
1·99	7·76	232	1·29	1·86	25·5	6·9
2·47	7·30	303	1·12	1·72	28·3	6·7
3·32	7·25	279	1·47	1·43	35·7	7·2
11·4	6·87	520	2·05	0·67	93·2	7·1
					best	6·7 ± 0·7
Solvent : *iso*Propylbenzene.						
0·96	9·49	231	1·13	2·35	19·0	7·6
1·66	7·84	232	1·26	1·84	25·7	8·4
3·08	8·00	330	1·45	1·40	36·6	8·1
6·22	8·68	449	1·90	0·92	63	8·2
					best	8·2 ± 0·6
Solvent : Diphenylmethane.						
0·65	14·5	185	2·16	1·79	26·7	23
1·33	17·9	281	2·63	1·26	42·0	23
					best	23 ±?
Solvent : Triphenylmethane.						
0·042	7·84	70	1·65	3·26	12·5	20
0·0446	11·38	142·5	1·12	3·11	13·2	33·6
0·0987	11·01	140·2	1·22	2·75	15·0	33·5
0·117	8·75	70	1·97	2·41	18·4	58
					best	35 ± 10

TABLE I.—(*Cont.*).

Solvent / Styrene (moles).	Yield (%).	Time (hr.).	k_2^a ($\times 10^4$).	$[\eta]^b$.	$1/P$ ($\times 10^5$).	C^e ($\times 10^5$).
Solvent : Fluorene.						
0·0343	7·31	111·6	0·85	1·33	39·2	802
0·0546	7·80	137·2	0·78	1·00	56·5	822
0·0605	6·99	95·1	0·99	1·00	56·2	735
					best	750 ± 50
Solvent : Pentaphenylethane.						
0·001	17·7	103	2·40	0·33	228	230,000
0·0123	20·8	114·5	2·60	0·075	2030	160,000
					best	200,000 ±?
Solvent : Decalin						
0·503	4·75	71·2	1·38	2·9	14·4	5·4
1·017	4·09	71·2	0·84	2·75	15·5	3·8
					best	4 ± 1
Solvent : *n*-Heptane.						
1·95	1·35	185	0·30	2·22	20·3	4·4
3·46	1·44	497	0·40	1·87	25·4	4·0
					best	4·2 ±?
Experiments at 100°.						
0·00	9·17	4·1	28·7	1·87	26·5 ($1/\overline{P}_0$)	
Solvent : Benzene.						
5·15	11·1	22·3	35·9	1·36	38·0	2·23
16·27	13·7	60·4	39·2	1·00	56·2	1·82
24·40	12·7	115·7	29·8	0·836	70·5	1·80
					best	1·84 ± 0·15
Solvent : Toluene.						
2·80	13·3	22·7	28·0	1·21	44·2	6·25
2·80	—	22·1	—	1·21	44·2	6·25
4·66	11·3	22·7	33·9	0·999	56·2	6·4
10·72	11·6	48·8	33·4	0·665	94·5	6·4
21·88	9·1	114·3	21·9	0·405	176	6·8
10·0	10·0	47·2	27·2	0·70[d]	89·0	6·3
					best	6·45 ± 0·3
Solvent : Ethylbenzene.						
0·47	10·78	7·3	29·1	1·48	33·8	15·5
1·06	9·64	9·6	27·5	1·22	43·9	16·4
1·92	12·63	16·3	30·4	1·01	55·7	15·2
4·01	11·21	24·1	31·6	0·677	92·2	16·4
9·10	18·27	91·4	30·2	0·411[e]	174	16·3
					best	16·2 ± 0·7
Solvent : *iso*-Propylbenzene.						
0·81	10·3	9·2	28·3	1·26[f]	42·0	19·1
1·10	10·7	11·1	28·8	1·14	50·1	21·4
1·44	11·1	13·1	29·9	1·03[g]	53·3	18·6
2·87	12·0	20·2	34·8	0·757[h]	80	18·7
6·02	16·8	45·3	42·4	0·449	155	21·4
					best	20·0 ± 1·2

TABLE I.—(*Cont.*).

Solvent / Styrene (moles).	Yield (%).	Time (hr.).	k_2[a] (× 10⁴).	$[\eta]$[b].	$1/P$ (× 10⁵).	C[c] (× 10⁵).
Solvent : Diphenylmethane.						
0·65	13·1	7·5	45·1	1·03	53·6 $(1/P_0)$	42 ± ?
Solvent : Triphenylmethane.						
0·0274	13·47	6·1	31·2	1·66	29·5	109
0·0486	13·77	7·1	28·3	1·63	30·1	75
0·052	11·0	5·4	29·3	1·63	30·1	70
0·082	12·25	5·4	34·6	1·52	33·0	79
					best	80 ± 30
Solvent : Fluorene.						
0·0313	10·86	6·1	24·3	0·89	65·3	1240 ± 150
Solvent : Cyclohexane.						
3·49	8·80	21·5	22·1	1·56	32·1	1·60
6·00	5·98	24·2	20·2	1·424	36·0	1·58
					best	1·6 ± 0·3
Solvent : *n*-Heptane.						
0·92	10·27	12·8	22·5	1·59	31·2	5·1
2·78	4·65	23·5	11·1	1·04	53·5	9·7
7·15	2·21	45·8	5·7	0·67	93·5	9·4
					best	9·5 ± ?
Solvent : *tert*-Butylbenzene.						
3·7	15·1	45·5	25	1·16	47·0	5·5 ± 1·5
Experiments at 132°.						
0·00	18·2	0·83	308	0·987[f]	56·8 $1/\bar{P}_0$	
0·00	10·80	0·73	200	0·99	56·7 $1/P_0$	
Solvent : Benzene.						
6·41	12·36	5·3	183	0·59	110	8·33
9·66	11·00	7·1	169	0·48	142	8·83
12·95	10·69	9·6	157	0·40	180	9·52
					best	8·9 ± 0·5
Solvent : Cyclohexane.						
4·76	9·82	3·5	197	0·663	95	8·05
6·96	10·84	5·5	191	0·542	122	9·4
					best	8·7 ± 0·8
Solvent : Ethylbenzene.						
0·75	8·24	0·83	224	0·83	71·5	20·0
1·36	10·24	1·4	227	0·67	93·8	27·2
3·15	11·63	3·0	193	0·46	152	30·3
					best	29 ± 5

a Second-order rate constants in l. mole⁻¹ hr.⁻¹.
b Intrinsic viscosity in benzene solution at 30°. See reference (3) for method.
c " Best value " is the slope of $1/\bar{P}$ against [SX]/[M] if plotted, otherwise is the weighted average of individual transfer constants with high dilution runs given the most weight. Estimated maximum error is weighted by number of experiments, precision, solvent range, and conformance of rate constants, k_2.
d–i Number average molecular weights determined osmometrically : *d*, 139,000 ; *e*, 50,600 ; *f*, 252,000 ; *g*, 177,000 ; *h*, 117,500 ; *i*, 171,000.

TABLE II.—TRANSFER CONSTANTS OF HYDROCARBONS WITH STYRENE.

Hydrocarbon.	Transfer Constant × 10^5.			$E_t - E_g$[a] (kcal./mole).	$\ln A_t/A_g$[a].
	60°.	100°.	132°.		
Benzene	0·16	1·84	8·9	14·8	9·06
tert-Butylbenzene	0·6	5·5		13·7	8·67
Toluene	1·25	6·45		10·1	4·03
Ethylbenzene	6·7	16·2	29	5·5	−1·27
iso-Propylbenzene	8·2	20·0		5·5	−1·09
Diphenylmethane	23	42		3·7	−2·76
Triphenylmethane	35	80		5·1	0·24
Fluorene	750	1240		3·1	0·19
Pentaphenylethane	200,000	—		—	
Cyclohexane	0·24	1·6	8·7	13·4	7·21
n-Heptane	4·2	9·5		5·0	−2·44
Decalin	4	—		—	
Carbon tetrachloride[a]	900	1810	3250	4·8	2·53

a Calculated from the Arrhenius equation, $C = Ae^{-E/RT}$, where $C = k_t/k_g$ is the transfer constant; E is the difference in activation energies for chain transfer and chain growth, E_t-E_g; A, the frequency factor, is the ratio A_t/A_g for the two processes.

Only the two most reactive hydrocarbons, fluorene and triphenylmethane, fail to fit eqn. (3). Carbon tetrachloride, in which transfer is not through a carbon-hydrogen bond, is not governed by the relation, and is not shown in Fig. 4.

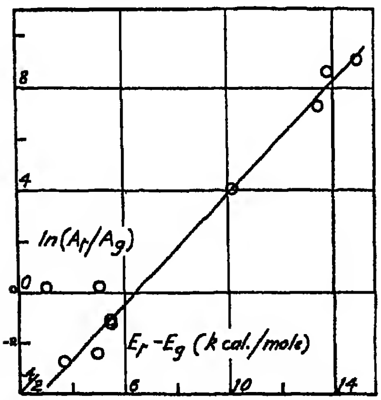

FIG. 4.—Relationship between activation energies and frequency factors for the transfer reaction of styrene radicals with hydrocarbons.

Correlations over smaller ranges of frequency factors and activation energies have been observed previously in non-radical reactions.[17] Several hypotheses have been advanced to explain such correlations, but no detailed discussion will be attempted at this time. It may be for this series that the experimental activation energies are lowered due to the decreased bond strengths in the presence of substituents and that the steric factors from the substituents also lower the frequency factor. The present dependency demonstrates the importance of both frequency factors and activation energies in free-radical reactions and points out the difficulties inherent in drawing relations between reaction rates, bond strengths, experimental activation energies, and frequency factors when either of the latter quantities is neglected.

The authors are indebted to Prof. P. Debye for opportunities to discuss the results of the present work.

Summary.

The effects of 12 hydrocarbons on the molecular weight of polymerising styrene, and hence their capacities to supply a hydrogen atom to a substituted

[17] Fairclough and Hinshelwood, *J. Chem. Soc.*, 1937, 538, 1573; Moelwyn-Hughes, *Kinetics of Reactions in Solution* (Oxford University Press, 1933), p. 167.

benzyl radical, have been determined. The ease with which a hydrogen atom can be removed from a carbon atom is increased appreciably by alkyl groups on the carbon atom, greatly by phenyl groups, and still more by an *o*-biphenylene group, fluorene being about 1000 times as reactive as cyclohexane.

From the effects of temperature on the hydrogen-transfer reaction, it is found that substitution on a carbon atom decreases the activation energy for hydrogen transfer, but also decreases the frequency factor so that the range in reactivity is much less than would be expected from the activation energies. A nearly linear relation between the experimental activation energy and the logarithm of the frequency factor for hydrogen transfer by these hydrocarbons has been found.

Résumé.

On a déterminé l'effet de 12 hydrocarbures sur le poids moléculaire du styrène polymérisant et, de là, leur capacité à fournir un atome d'hydrogène à un radical benzyle substitué. La facilité avec laquelle un atome d'hydrogène est séparé d'un atome de carbone, est accrue sensiblement par des groupes alcoyle sur l'atome de carbone, beaucoup par des groupes phényle, et encore plus par un groupe *o*-diphénylène, le fluorène étant environ 1000 fois plus réactif que le cyclohexane. La substitution sur un atome de carbone diminue l'énergie d'activation par le transfert d'hydrogène, mais aussi diminue le facteur de fréquence, si bien que la variation de réactivité est inférieure à celle qu'on attendrait d'après les énergies d'activation. On trouve une relation presque linéaire entre l'énergie d'activation expérimentale et le logarithme du facteur de fréquence pour le transfert d'hydrogène par ces hydrocarbures.

Zusammenfassung.

Der Effekt von 12 Kohlenwasserstoffen auf das Molekulargewicht bei der Polymerisation von Styrol und daher deren Fähigkeit, ein Wasserstoffatom an ein substituiertes Benzylradikal abzugeben, ist bestimmt worden. Die Leichtigkeit, mit der ein Wasserstoffatom von einem Kohlenstoffatom entfernt werden kann, wird durch Äthylgruppen an diesem C-atom merklich erhöht, in grösserem Ausmasse durch Phenylgruppen und noch mehr durch eine *o*-Diphenylengruppe ; z.B. ist Fluoren 1000 mal wirksamer als Cyclohexan. Substitution an einem C-Atom vermindert sowohl die Aktivierungsenergie als auch die Aktionskonstante für die Wasserstoffübertragung, sodass das Bereich der Reaktivitäten kleiner ist als man aus den Aktivierungsenergien allein schliessen würde. Es besteht eine fast lineare Beziehung zwischen der experimentellen Aktivierungswärme und dem Logarithmus der Aktionskonstante für die Wasserstoffübertragung durch diese Kohlenwasserstoffe.

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THE REACTIVITY OF FREE RADICALS IN POLYMERISATION REACTIONS.

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Considerable information is available concerning the effect of structure on the reactivity of different organic substances with free radicals. For example, studies of the reactivity of primary, secondary, and tertiary hydrogen atoms attached to carbon,[1] of α-methylene hydrogen atoms in unsaturated substances,[2] of solvents [3] and of vinyl monomers [4] have been made. On the other hand, very little is known concerning the relative

[1] Smith and Taylor, *J. Chem. Physics*, 1939, 7, 390.
[2] (*a*) Criegie, Pilz, and Flygare, *Ber*,. 1939, 72, 1799 ; (*b*) Farmer, *et al.*, *J. Chem. Soc.*, 1942, 121, 513. [3] Mayo, *J. Amer. Chem. Soc.*, 1943, 65, 2324.
[4] Nozaki, *J. Polymer Sci.*, 1946, 1, 455.

reactivity of different free radicals in such reactions. The work of Kharasch, Kane and Brown,[5] in which radicals were divided into two classes according to their ability to abstract chlorine atoms from carbon tetrachloride, represents perhaps the most important contribution in this direction. In the present paper an attempt is made to correlate radical reactivities, utilising results from studies of polymerisation and related reactions.

The importance of resonance stabilisation in influencing the reactivity of free radicals is generally accepted; [6] stabilised radicals are considered to be less reactive than unstabilised ones. If it is assumed that the relative reactivity of substituted methyl free radicals is determined for the most part by the amount of resonance stabilisation,[7] knowledge of an order of substituents according to their ability to promote such stabilisation would enable one to predict relative radical reactivity. We now suggest that such an order has been obtained from copolymerisation experiments, where the amount of resonance stabilisation imparted by substituents on methyl free radicals appears to be the most important factor governing the general order of reactivity of monomers in the propagation reaction.[4] This order of substituents on a methyl radical according to ability to promote resonance stabilisation is as follows:

$$(C_6H_5) > (CH{=}CH_2{}^*) > (CN) \cong (COOCH_3) > (Cl) > (CH_2R) \cong (O_2CCH_3) > (H).$$

Thus, $\cdot CH_2{-}CH{=}CH_2$ or $\cdot CH_2C_6H_5$ should be more stabilised and less reactive than $\cdot CH_2Cl$ or $\cdot CH_2{-}CH_2R$, and the unsubstituted methyl radical should be most reactive. It is assumed, further, that the order holds additively for a second and third substituent on the methyl radical.

The above interpretation of radical reactivity is in agreement with existing data such as the low reactivity of triphenyl methyl and allyl radicals,[6] the reactivity grouping of Kharasch, Kane and Brown,[5] and the evidence that the methyl radical is more reactive then the undecyl radical.[8] We shall now attempt to show that this order of radical reactivity will explain certain chain-transfer results observed during polymerisation reactions.

Chain Transfer Involving Monomers.

Most monomers with α-methylene hydrogens do not polymerise well by a free-radical reaction. For example, allyl acetate,[6b] octene-1,[9] propylene,[10] *iso*butylene [11] and *iso*propenyl acetate [11] polymerise with difficulty to give low molecular weight materials. This is undoubtedly due to the ready abstraction of α-methylene hydrogen atoms by the growing polymer radicals, resulting in the formation of allyl-type radicals which, because of their stability, have difficulty in carrying on the polymerisation chain.

On the other hand, the α-methyl containing monomers, methyl methacrylate [12] and methacrylonitrile,[13] polymerise to high molecular weight

[5] Kharasch, Kane and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 1621.

[6] (*a*) Waters, *Trans. Faraday Soc.*, 1941, **37**, 770; (*b*) Bartlett and Altschul, *J. Amer. Chem. Soc.*, 1945, **67**, 816; (*c*) Taylor and Smith, *J. Chem. Physics*, 1940, **8**, 543.

[7] Polarity and steric effects may sometimes be important in free radical reactions (Ref. 4 and Price, *J. Polymer Sci.*, 1946, **1**, 83).

* The positions of $CH{=}CH_2$ and C_6H_5 in the original order [4] have been interchanged because the presence of two equivalent vinyl groups in butadiene was overlooked previously.

[8] Kharasch, Jensen and Urry, *J. Org. Chem.*, 1945, **10**, 388.

[9] Kharasch, Reinmuth and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1105.

[10] Beeck and Rust, *J. Chem. Physics*, 1941, **9**, 480.

[11] Unpublished experiments by the author.

[12] (*a*) Norrish and Smith, *Nature*, 1942, **150**, 336; (*b*) Baxendale, Evans and Kilham, *J. Polymer Sci.*, 1946, **1**, 466.

[13] Kern and Fernow, *J. pr. Chem.*, 1942, **160**, 276.

polymers with no evidence of chain transfer. Similarly, the dienes, isoprene and 2 : 3-dimently-butadiene-1 : 3,[14] can be polymerised to high molecular weight products. The difference in behaviour between these monomers and those listed above is understandable in terms of our radical stabilisation series. The growing polymer radicals formed from the poorly polymerisable monomers are all substituted methyl radicals with substituents low in the stabilisation series. Thus, the reactivity of the radicals is high and they can readily abstract hydrogen atoms from α-methylene groups. On the other hand, the polymer radicals from methyl methacrylate, methacrylonitrile, and the two dienes are so well stabilised by a substituent high in the series that α-methylene hydrogen abstraction is small or absent.

Among the monomers which would be expected to form very reactive radicals, only ethylene, vinyl acetate and vinyl chloride polymerise completely or nearly so with small concentrations of peroxide-type initiators. It is interesting to note that, during polymerisation, chain transfer with the monomer [15] appears to occur with all three monomers. This is suggested by the failure of the molecular weight of polyvinyl acetate [16] and polyethylene [17] to increase beyond a certain value with decreasing catalyst concentration, and the constancy of the molecular weight of polyvinyl chloride samples prepared utilising different methods [18] and rates [19] of initiation. In contrast to this, it appears that monomers such as styrene,[20] methyl methacrylate,[18] methacrylonitrile [18] and ethyl acrylate,[21] which should form more stabilised radicals, undergo very little, if any, chain transfer of this type. This, too, could be attributed to differences in the reactivity of polymer radicals due to resonance stabilisation.

Chain Transfer Involving Solvents.

When a monomer is polymerised by a free-radical process in the presence of a solvent, the molecular weight of the product is generally lower than if the reaction had been carried out with pure monomer. This has been shown to be the result of chain trasfer with the solvent.[22] The amount of chain transfer with a given monomer at a fixed temperature varies from solvent to solvent, and Mayo [22a] has used the chain-transfer constant, C, defined as the rate constant for chain transfer with the solvent divided by the rate constant for chain growth, to show this difference in styrene polymerisation. It is found that the constant also differs from monomer to monomer, as is illustrated by the data in Table I. The values of the constant are much smaller for styrene than those for either vinyl acetate or allyl acetate.

Similar results of a more qualitative nature are found in two recent papers by Kharasch and co-workers.[23] They found that, when an ethylene derivative, carbon tetrachloride and a free-radical type initiator are mixed and heated, the following reaction occurs

$$n\mathrm{RCH{=}CH_2 + CCl_4 \rightarrow Cl(RCHCH_2)_nCCl_3}$$

[14] Starkweather, *et al.*, *Ind. Eng. Chem.*, 1947, 39, 210.
[15] Flory, *J. Amer. Chem. Soc.*, 1937, 59, 241.
[16] Cuthbertson, Gee and Rideal, *Proc. Roy. Soc.*, *A*, 1939, 170, 300.
[17] Hopff and Kern, *Modern Plastics*, 1946, 23, 160.
[18] Mead and Fuoss, *J. Amer. Chem. Soc.*, 1942, 64, 277.
[19] Unpublished experiments by the author.
[20] Staudinger and Huseman, *Ber.*, 1935, 68, 1691.
[21] Staudinger and Trommsdorff, *Annalen*, 1933, 502, 201.
[22] (*a*) Mayo, *J. Amer. Chem. Soc.*, 1943, 65, 2324; (*b*) Kamenskaya and Medvedev, *Acta Physicochim.*, 1940, 13, 565.
[23] (*a*) Kharasch, Jensen and Urry, *J. Amer. Chem. Soc.*, 1947, 69, 1100; (*b*) Kharasch, Reinmuth and Urry, *ibid.*, 1947, 69, 1105.

n being often equal to one. This is undoubtedly the result of a chain process during which the following reactions proceed:

$$RCH{=}CH_2 + \cdot CCl_3 \rightarrow \cdot(CHRCH_2)CCl_3 \quad (1)$$

$$\cdot(CHRCH_2)CCl_3 + RCH{=}CH_2 \rightarrow \cdot(CHRCH_2)_2CCl_3 \quad (2)$$

$$\cdot(CHRCH_2)_nCCl_3 + RCH{=}CH_2 \rightarrow \cdot(CHRCH_2)_{n+1}CCl_3 \quad (3)$$

$$\cdot(CHRCH_2)_nCCl_3 + CCl_4 \rightarrow Cl(CHRCH_2)_nCCl_3 + \cdot CCl_3. \quad (4)$$

It is apparent that the reaction is related to polymerisation involving chain transfer with the solvent. When different monomers are treated under similar conditions, it is found that ethylene,[22a] propylene,[22a] biallyl,[22a] *iso*-butylene[24] and vinyl acetate[24, 25] readily give the carbon tetrachloride addition product with $n = 1$, allyl chloride[8, b] gives a product with $n = 2$, and styrene,[22a] ethyl acrylate[22a] and dienes[24, 26] give polymers (i.e. n is large).

TABLE I.—CHAIN-TRANSFER CONSTANTS FOR SEVERAL MONOMER-SOLVENT COMBINATIONS AT 80° C.

Monomer.	Solvent.	$C \times 10^5$.
Styrene[a]	Toluene	3·13
Vinyl acetate[b]	Toluene	916
Styrene[a]	Benzene	1·56
Allyl acetate[c]	Benzene	210
Styrene[a]	Cyclohexane	1·56
Allyl acetate[c]	Cyclohexane	560

(*a*) Calculated from the results of Mayo[22a] using the Arrhenius equation.
(*b*) Calculated from data of Cuthbertson, Gee and Rideal.[16]
(*c*) Unpublished results of Bartlett and Nozaki.

The above results, which indicate that chain transfer with a solvent occurs much more readily during the polymerisation of a monomer which would be expected to form a relatively unstabilised radical than during the polymerisation of a monomer yielding a more stabilised one, can be the result of a difference in the values of the rate constant of one or both of two reactions. These are (1) the propagation reaction in polymerisation, and (2) the attack of the growing polymer-radical on the solvent.

If the propagation reaction is much faster with conjugated monomers than with unconjugated ones, the chain-transfer results in solvents could be readily explained. Indeed, this is actually the case in copolymerisation, where conjugated monomers add more readily to a given radical than unconjugated ones.[4]. The situation, however, is quite different when one is comparing the propagation rate constant of one pure monomer against another. Here, the growing polymer radicals differ in the two systems, and a conjugated monomer would yield a more stabilised and, hence, less reactive radical than an unconjugated monomer. Thus, it is probable that the lower reactivity of an unconjugated monomer in the propagation reaction would be roughly compensated by an increase in the reactivity of the polymer radical derived from it.[27]

The discussion above leads to the conclusion that the chain-transfer results are most probably attributable to differences in the ability of different radicals to attack the solvent and abstract hydrogen or chlorine atoms. In this connection it is interesting to note that the results in

[24] Urry, Conference on *Organic Reaction Mechanisms*, Notre Dame University, Sept. 3-6, 1946.
[25] Harmon (to Du Pont), U.S. Patent 2,396,261 (1946).
[26] Under special conditions good yields of the product with $n = 1$ may be obtained from butadiene [Peterson (to Du Pont), U.S. Patent 2,401,099 (1946)][4]
[27] The results of Bartlett and Altschul,[43] which indicate that stabilised allyl-type radicals are much less effective in carrying on the polymerisation of allyl acetate than the growing polymer radicals, show that the rate constant for the propagation reaction must be dependent on the reactivity of the free radical involved.

Table I show that chain transfer with solvents occurs 135 to 360 times more readily with allyl acetate or vinyl acetate than with styrene, whereas copolymerisation studies [4] indicate that styrene is only about 36 times as reactive as allyl acetate or vinyl acetate in the propagation reaction with a given radical. Thus, even if the assumption were made that the rate constant for the propagation reaction during polymerisation is independent of the reactivity of the free radicals involved, the conclusion that the growing-polymer free-radicals derived from allyl acetate or vinyl acetate are more reactive with solvents than those derived from styrene is still necessary. All of the results discussed are in agreement with the proposed order of substituents promoting resonance stabilisation in substituted methyl radicals; i.e. radicals with substituents effective in promoting stabilisation are relatively ineffective in chain transfer and, conversely, radicals with substituents ineffective in promoting stabilisation are relatively effective in chain transfer.

Chain Transfer Involving Hydrochloric Acid.

A reaction closely related to those discussed in the preceding section has been disclosed in a recent patent.[28] When ethylene, hydrochloric acid and a free-radical type initiator are heated under high pressure, the following reaction occurs

$$n(CH_2{=}CH_2)+HCl \rightarrow H(CH_2CH_2)_nCl.$$

The reaction mechanism probably involves the following steps:

$$\text{Initiator} \rightarrow \cdot R \qquad (1)$$
$$\cdot R+HCl \rightarrow RH+\cdot Cl \qquad (2)$$
$$\cdot Cl+CH_2{=}CH_2 \rightarrow \cdot(CH_2CH_2)Cl \qquad (3)$$
$$\cdot(CH_2CH_2)Cl+CH_2{=}CH_2 \rightarrow \cdot(CH_2CH_2)_2Cl \qquad (4)$$
$$\cdot(CH_2CH_2)_nCl+CH_2{=}CH_2 \rightarrow \cdot(CH_2CH_2)_{n+1}Cl \qquad (5)$$
$$\cdot(CH_2CH_2)_nCl+HCl \rightarrow H(CH_2CH_2)_nCl+\cdot Cl \qquad (6)$$

When $n = 1$, the chain-carrying steps in the reaction are (3) and (6). It is evident, at once, that this chain process is identical to that suggested for the abnormal addition of hydrobromic acid to ethylene derivatives,[29] except that hydrochloric acid has replaced the hydrobromic acid.

This is apparently the first and only reported case of the addition of hydrochloric acid to an ethylene derivative by a free-radical mechanism. Why is this so? Step (3) is exothermic by over 30 kcal. per mole but step (6) is endothermic by about 5 kcal. and is probably the critical step in the chain. Resonance stabilisation in the radical would, by increasing the activation energy for the reaction, decrease the rate constant for step (6). Thus, the probability of observing hydrochloric acid addition via a free-radical chain reaction should be greatest with the ethylene derivative forming the least stabilised radical in step (3). Our radical stabilisation series predicts that this should be ethylene. It is noteworthy that the patent of Hanford and Harmon [28] applies only to ethylene, suggesting that the reaction will not occur satisfactorily or at all with other ethylene derivatives.

Summary.

It is assumed that the relative reactivity of substituted methyl free radicals is determined for the most part by the resonance stabilisation of the radicals and that an order of substituents determined from copolymerisation experiments predicts qualitatively the amount of this stabilisation. The order of substituents favouring resonance stabilisation is as follows:

$$(C_6H_5) > (CH{=}CH_2) > (CN) \cong (COOCH_3) > (Cl) > (CH_2R) \cong (O_2CCH_3) > (H).$$

[28] Hanford and Harmon (to Du Pont), U.S. Patent 2,418,832 (1947).
[29] Mayo and Walling, *Chem. Rev.*, 1940, 27, 372.

Utilising this order, certain chain transfer results observed during polymerisation reactions are discussed. They include (1) chain transfer involving monomers, (2) chain transfer involving solvents and (3) chain transfer involving hydrochloric acid.

Résumé.

On suppose que les réactivités relatives de radicaux libres méthyle substitués sont déterminées en majeure partie par la stablisation de résonance des radicaux et que les substituants, classés d'après des expériences de copolymérisation, permettent de donner l'order de grandeur de cette stablisation. L'ordre des substituant favorisant la stablisation de résonance est le suivant :

$$(C_6H_5) > (CH{=}CH_2) > (CN) \cong (COOCH_3) > Cl > CH_2R \cong (O_2CCH_3) > H.$$

S'appuyant sur ce classement, on discute certains résultats de transferts de chaînes, observés au cours de reáctions de polymérisation. Il s'agit de transferts de chaînes comprenant (1) des monomères, (2) des solvants et (3) HCl.

Zusammenfassung.

Es wird angenommen, dass die relative Reaktivität von freien substituierten Methylradikalen haupsächlich von der Resonanzstabilisierung der Radikale bedingt ist und dass der Betrag dieser Stabilisierung in qualitativer Weise aus Kopolymerisationsversuchen abgeleitet werden kann. Die Reihenfolge, in welcher Substituenten die Resonanzstabilisierung begünstigen, ist wie folgt :

$$(C_6H_5) > (CH{=}CH_2) > CN \cong (COOCH_3) > Cl > CH_2R \cong (O_2CCH_3) > H.$$

Unter Benützung dieser Aufstellung werden bestimmte Kettenübertragungsresultate, die in Polymerisationsreaktionen beobachtet wurden, besprochen, darunter Kettenübertragungen, die (1) Monomeren, (2) Lösungsmittel und (3) HCl betreffen.

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THE INHIBITION AND RETARDATION BY CERTAIN QUINONES OF THE PEROXIDE-INDUCED POLYMERISATION OF ALLYL ACETATE AND VINYL ACETATE.

By Paul D. Bartlett, George S. Hammond and Harold Kwart.

Received 11*th August*, 1947.

Substances which, while present in a polymerisable monomer, produce an apparently-complete arrest of its polymerisation have been designated as inhibitors, while substances which permit polymerisation to proceed at a diminished rate are commonly called retarders. The boundary between these classes of compounds shifts with refinement of the method of observation ; for it becomes apparent with the use of sensitive methods that even the so-called inhibitors do not always stop all participation of the monomer in the reaction. As far as mechanisms of reaction are concerned there need be no significant difference between inhibitors and retarders.

It is generally agreed that inhibition or retardation of a chain reaction is produced by interception and removal of the free radical which carries the chain. The existence of a rapid mode of consumption of the radical lowers its concentration at the steady state and hence lowers in proportion the rates of all the reactions dependent upon the concentration of free

radicals. If this lowering is great, the substance is likely to be called an inhibitor; if the lowering is quantitatively less, the substance is called a retarder.

The process of retardation is at its simplest in principle when the retarder is itself a stable free radical. In such a case there need be but a single elementary act in the inhibitory process, namely, the union of the retarder with the chain carrier to produce a stable molecule. Examples of this ideal case are comparatively rare; they include the use of nitric oxide as an inhibitor of cracking [1] and other gas-phase reactions, and, in another part of the present programme of research, the inhibition of polymerisation of vinyl acetate by 2 : 2-diphenyl-1-picrylhydrazyl. The scarcity of examples of this simplest form of inhibition is due largely to the fact that few free radicals are so stable that they will not initiate chain reactions to some extent, thus blurring the picture of the phenomenon which it is desired to observe. (Triphenylmethyl, for example, can act as both an initiator and a retarder of polymerisation of styrene, with resulting complication of the kinetic picture.) [2]

Whenever a retarder is not a free radical but a molecule, a mechanism must take account not only of the reaction of the chain carrier with the retarder molecule but of the subsequent behaviour of the new radical so formed. It is obvious that this new radical must be less active than the original chain carrier with respect to chain propagation, but we may expect to find as much variation from case to case in this regard as in the overall effectiveness of inhibitors and retarders, and the mechanism is not complete until the eventual conversion of each radical into a stable molecule has been accounted for. The general principles of reaction mechanisms lead one to anticipate several possibilities, which may be outlined as follows.

A. In the attack on the chain carrier, the retarder may
   1. combine by direct addition;
   2. react by transfer of an atom (or group) to or from the chain carrier, producing a molecule and a fragment coming from the retarder.

B. In either case the following possibilities must be considered for the disposal of the new free radical formed.
   1. Union with another free radical
      (*a*) with a radical like itself (dimerisation),
      (*b*) with a second chain carrier.
   2. Reaction by transfer of an atom (or group)
      (*a*) with a radical like itself (disproportionation),
      (*b*) with a second chain carrier,
      (*c*) with another retarder molecule, producing a further radical.
   3. Union with a molecule (chain propagation)
      (*a*) with a monomer,
      (*b*) with a retarder

(copolymerisation in Case A1, chain transfer in Case A2).

C. The molecules produced by these processes may be
   1. inert,
   2. initiators,
   3. retarders,
   4. chain-transfer agents,
   5. substances entering into copolymerisation.

The minimum satisfactory description of the mechanism of action of an inhibitor or retarder would consist of placing it in its proper class with

[1] Echols and Pease, *J. Amer. Chem. Soc.*, 1938, 60, 1701; for other references see Steacie, *Atom and Free Radical Reactions* (New York, 1946), pp. 58-61.

[2] Unpublished observations in this laboratory.

respect to all three of these stages of the process. We have carried out a study of various types of inhibitors and retarders, including free radicals, iodine, oxygen, sulphur, quinones, nitro compounds, disulphides, and *N*-bromosuccinimide, and have been partially successful in establishing the nature of the retarding process in certain cases. At the same time we have been impressed with the great variations among the different compounds studied. At this time we report the study of one class of such compounds, the quinones.

Two monomers have been employed in this study, allyl acetate and vinyl acetate. The former ester was chosen because its very short chain length [3] in polymerisation should cause a relatively large number of inhibitor fragments to become attached to the polymer and it was hoped that direct evidence could be gained of the chemical nature of these groups. Vinyl acetate, on the other hand, polymerises to long chains and lends itself better to studies of kinetics than of the nature of the end groups. Four quinones—benzoquinone, trichloroquinone, chloranil, and duroquinone—were chosen for study, covering as they do a range of degree of substitution, oxidation potential, and chemical character of groups.

Chemical Nature of the Inhibitor Fragments in the Polymer.—Suggestions have been made in the past as to the mechanism of quinone-inhibited polymerisation. Price [4] suggested the sequence A1-B2*b* for inhibition by benzoquinone, and later [5] modified this to A1-B2*c*; the consequence that the polymer should contain alkylquinone groups seems to be borne out by the observations of Cohen [6] on the quinone-inhibited polymerisation of styrene. Foord, [7] on the other hand, found that phenanthraquinone had inhibitory powers of the same order as benzoquinone, although nuclear substitution by radicals could scarcely occur by similar mechanisms in the two cases. Although we could not isolate any recognisable compound from the polyallyl acetate containing the quinone group, some evidence of the nature of such groups was obtained by pyrolysis, cleavage with hydrogen iodide, and observation of the absorption spectrum of the product.

When chloranil and benzoyl peroxide were heated in allyl acetate under the conditions of the kinetic runs, no quinone was recovered and the solutions showed no quinone by titration. Alkali extraction and adsorption yielded no pure compound except benzoic acid. There was a little volatile chlorine-containing compound boiling higher than allyl acetate and melting below room temperature and a small alkali-soluble fraction of the polymer which gave an amorphous 2 : 4-dinitrophenylhydrazone. Such a product of retarded polymerisation yielded tetrachlorohydroquinone on destructive distillation under diminished pressure at 360° (yield of recrystallised product, 20 %). A somewhat higher yield, 27 %, of tetrachlorohydroquinone was obtained by cleaving the polymer with hydriodic acid in refluxing acetic acid. By this treatment there was also obtained colourless polymeric material which could be oxidised to a yellow oil, reducible again with stannous chloride or zinc dust, but not with iodide. These results are consistent with the view that the quinone is all bound in the polymer, some of it through carbon and some—at least 27 %—through oxygen with the four chlorine atoms intact.

The ultraviolet absorption of the product of a polymerisation of allyl acetate initiated by benzoyl peroxide and retarded by benzoquinone was examined and the curve is reproduced in Fig. 1, together with a similar spectrum of the product of heating the same amounts of benzoyl peroxide and benzoquinone in cyclohexane as solvent. The values of log ϵ are

[3] Bartlett and Altschul, *J. Amer. Chem. Soc.*, 1945, **67**, 812, 816.
[4] Price, *Ann. N.Y. Acad. Sci.*, 1943, **44**, 368.
[5] Price, *Reactions at Carbon-Carbon Double Bonds* (New York, 1946), p. 86.
[6] Cohen (in press).
[7] Foord, *J. Chem. Soc.*, 1940, 48.

assigned on the assumption that the molar concentration of the absorbing material is the same as that of the original quinone. For comparison there are included in Fig. 1 the absorption curves of hydroquinone dimethyl ether, hydroquinone diphenyl ether, and *p*-xyloquinone, as models of products in which the quinone has been alkylated on oxygen and on carbon. It is clear that none of the model substances reproduces the curve of either product at all closely. In particular the product lacks any absorption

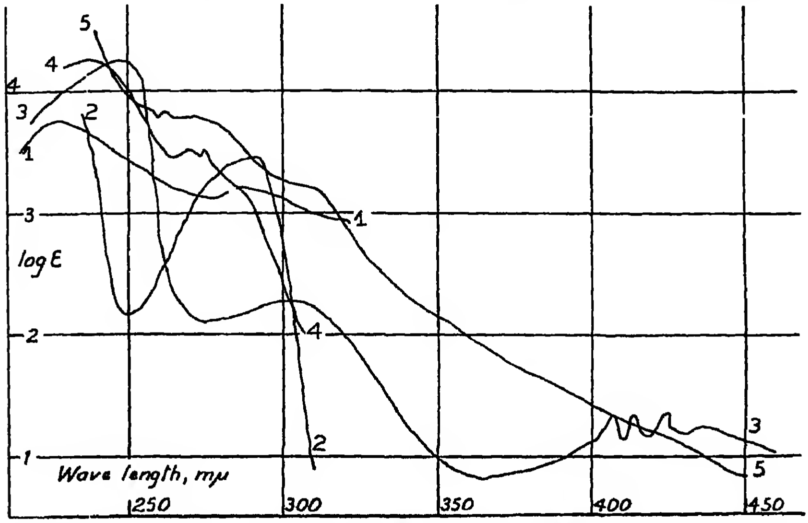

Fig. 1.—Absorption spectra of polymerisation products and model compounds (1) Product of heating benzoyl peroxide and quinone in cyclohexane, conditions like those in the sample of Curve 5; spectrum determined in alcohol-chloroform. (2) Hydroquinone diphenyl ether.* (3) *p*-Xyloquinone.[8] † (4) Hydroquinone diphenyl ether.‡ (5) Product of heating 0·257 M. peroxide and 0·127 M. benzoquinone in allyl acetate for 48 hrs. at 90°. The portion of the curve from 240 to 320 mμ was determined in ethanol-chloroform solvent; that from 320 to 450 mμ in chloroform. The difference of 0·2 in log ε between the two samples at 320 mμ was added to the chloroform curve as a constant correction to yield a continuous curve.

maximum in the region 400-440 mμ, characteristic of the quinone chromophore. Taken in combination with the other evidence cited, these results show that the product of the quinone-retarded polymerisation contains more than one type of transformation product of the quinone nucleus. These transformations almost certainly include alkylation on carbon and on oxygen, and also other changes resulting in more intense absorption at and above 300 mμ than is characteristic of any of the model substances here considered. It is worth noting that the intensity of absorption does not vary much with successive alkylation of the quinone from benzoquinone to *p*-xyloquinone.[8]

Kinetic Studies with Allyl Acetate.—Interest in the kinetic studies centres about the relation between the concentrations of three species, the initiator, the monomer, and the retarder. All three concentrations have been followed separately in these experiments with allyl acetate. The unsaturation, indicating the concentration of monomer, was followed as in previous studies with allyl acetate.[9] Benzoyl peroxide and the quinones are all oxidising substances, but it was found possible

[8] Light, *Z. physik. Chem. A*, 1926, **122**, 427.
* Wolf and Herold, *Z. physik. Chem., B*, 1931, **13**, 201.
† From ref. 8. ‡ Mayer-Pitsch, *Z. Elektrochem.*, 1943, **49**, 370.

in the cases of benzoquinone and duroquinone to make a satisfactorily quantitative separation between the peroxide and quinone by precipitation of the former from glacial acetic acid solution with water. The two oxidants were then titrated separately.

It was observed by Nozaki and Bartlett [9] that antioxidants and retarders of polymerisation also diminished the overall rate of decomposition of benzoyl peroxide in acetic anhydride as solvent. Cohen, on the other hand,[10] finds evidence of acceleration of the decomposition of benzoyl peroxide by benzoquinone in styrene. In the course of the present work it was found that the solutions containing both benzoyl peroxide and benzoquinone in allyl acetate underwent a fairly rapid change in the light involving loss of the oxidising power of the quinone and the formation of another effective retarder of polymerisation. Only when this disturbing process was prevented by operating in "low-actinic" Pyrex tubes was it possible to obtain reproducible measurements of polymerisation and the consumption of peroxide and quinone. Under these conditions the decomposition of peroxide was apparently of the first order and proceeded in a 12 % solution of peroxide in the presence of benzoquinone or a 4·8 % solution of peroxide in the presence of duroquinone at 80° with the same rate constant of 0·133 hr.$^{-1}$.

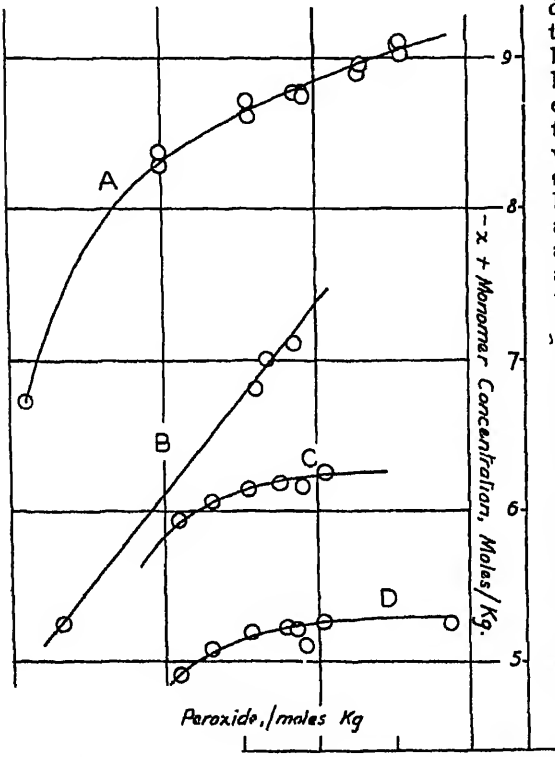

FIG. 2.—Monomer concentration against peroxide concentration for polymerisation of allyl acetate at 80° in the presence of benzoyl peroxide and several quinones. To avoid confusion of points, the curves are displaced vertically by amounts, x. A, benzoquinone, 0·257 M., $x = 0$; B, duroquinone, 0·100 M., $x = 2$; C, trichloroquinone, 0·105 M., $x = 3$; D, chloranil, 0·104 M., $x = 4$.

In the absence of retarder, Bartlett and Altschul [8] found apparent unimolecular rate constants of 0·235 hr.$^{-1}$ and 0·227 hr.$^{-1}$ for 9·95 % and 6·10 % benzoyl peroxide, respectively. It is clear, therefore, that in allyl acetate these two quinones exert an inhibitory effect upon the induced decomposition of benzoyl peroxide.

The precipitation method by which benzoyl peroxide and benzoquinone were separated for titration was unsuccessful with trichloroquinone and chloranil, but it was observed that at similar initial concentrations of peroxide, the late points (after complete consumption of the quinone)

[9] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, 68, 1686.
[10] Cohen, *J. Amer. Chem. Soc.*, 1947, 69, 1057.

showed the same peroxide concentrations in the runs made with the chloroquinones as in the runs with benzoquinone and duroquinone. It follows that the rate of decomposition of peroxide must have been the same in the presence of all four quinones, and we are justified in using the rate constant for peroxide decomposition, measured with benzoquinone, to calculate the concentrations of benzoyl peroxide at successive times in the runs with the chlorinated quinones. These values, in conjunction with the total oxidising titres, yielded the concentrations of quinone at different times.

During the polymerisation of allyl acetate without a retarder present, a linear relationship is maintained between the concentrations of monomer and peroxide.[8] In the polymerisation of styrene, the presence of benzoquinone produces a period of apparently total inhibition followed by polymerisation at nearly the same rate as in the absence of inhibitor.[7, 10] Fig. 2 shows typical curves of monomer-peroxide concentration in the presence of each of the quinones studied. In no case is total inhibition observed. With chloranil and trichloroquinone there is strong initial retardation and little monomer converted to polymer; as the peroxide decomposition proceeds the polymerisation increases and the effectiveness of a peroxide molecule in polymerising monomer approaches that observed in the absence of quinone. With duroquinone in the same concentration range the plot of M against P remains a straight line of lower slope than in the absence of retarder. Benzoquinone at low concentrations gives a curve like that of the chlorinated quinones, while at a concentration of 0·500 it yields a straight line corresponding to substantial retardation by a retarder whose concentration is not altered seriously during the run.

Comparison of the four quinones illustrates the general property of retarded reactions that the strongest retarders are the most rapidly used up, and give the sharpest change of rate between the early and late parts of the reaction.

Quantitative Measurement of Inhibitory Activity.—Introducing a simple one-step retardation into the scheme previously written[8] for allyl acetate polymerisation, we arrive at the following mechanism in which P denotes peroxide, M monomer, R free radical, I retarder or inhibitor, and X and Y inactive products:

$$\begin{aligned} \mathrm{P} &\xrightarrow{k_1} 2\mathrm{R} \\ \mathrm{R} + \mathrm{M} &\xrightarrow{k_2} \mathrm{R} \\ \mathrm{R} + \mathrm{M} &\xrightarrow{k_3} \mathrm{X} \\ \mathrm{R} + \mathrm{I} &\xrightarrow{k_4} \mathrm{Y} \end{aligned}$$

According to this mechanism there should be a simple relationship between the rates of disappearance of monomer and of retarder. Since

$$-\frac{dI}{dt} = k_4 IR$$

and

$$-\frac{dM}{dt} = (k_2 + k_3)MR,$$

it follows that

$$\frac{dI}{dM} = \frac{k_4}{k_2 + k_3}\frac{I}{M},$$

and

$$\ln\frac{I_0}{I} = \frac{k_4}{k_2 + k_3}\ln\frac{M_0}{M}.$$

In testing this relationship it is found to be obeyed closely by duroquinone and not at all by benzoquinone. Trichloroquinone and chloranil yield straight lines when log I is plotted against log M, but there is so little change in monomer concentration that a rigorous test of the equation is not afforded in these two cases. From the slopes of the straight lines

in the cases of duroquinone, chloranil and trichloroquinone, values of $k_4/(k_2 + k_3)$ have been determined and are recorded in Table I. Constants for benzoquinone have been estimated from the initial slopes of the curves.

TABLE I.—INHIBITION CONSTANTS OF QUINONES IN ALLYL ACETATE

Inhibitor	P_0 in Moles/kg.	I_0 in Moles/kg.	$k_4/(k_2 + k_3)$
Benzoquinone .	0·500	0·500	46
,, .	0·257	1·257	57
,, .	0·254	0·127	62
,, .	0·200	0·100	46
,, .	average	value	52
Chloranil . .	0·206	0·104	160
Trichloroquinone .	0·207	0·105	55
Duroquinone .	0·202	0·101	4·14

These ratios are a direct measure of the relative probability of a chain-carrying radical reacting with a quinone molecule in preference to reacting with a monomer by addition or by degradative chain transfer.

The above equation can also be applied to the data of Breitenbach and Breitenbach [11] on the inhibition of thermal polymerisation of styrene by certain quinones. In each case the plot of log M-log I is linear or nearly so; the slopes yield values of k_4/k_2 as recorded in Table II. From

TABLE II.—INHIBITION CONSTANTS FOR STYRENE FROM BREITENBACH'S DATA.

Quinone	k_4/k_2	log k_4/k_2 [b] + 1·000	E^0
Chloranil . .	950	3·98	0·657
Benzoquinone [a] .	566	3·76	0·570
Toluoquinone .	210	3·33	0·528
p-Xyloquinone .	43	2·64	0·486
Trimethylquinone .	26	2·42	0·444
Duroquinone .	0·67	0·83	0·402

(a) Only one point reported.
(b) Styrene monomer does not disappear by k_3.

a comparison of Tables I and II, it is seen that duroquinone is a stronger inhibitor for allyl acetate polymerisation than for styrene polymerisation, while benzoquinone and chloranil are stronger inhibitors for styrene than for allyl acetate.

The values of log k_4/k_2 determined in this way do not show the strictly linear relation to the oxidation potentials of the quinones which were observed for the logarithm of the standard rate of inhibited polymerisation evaluated by Breitenbach and Breitenbach. Fig. 3 shows the values of log k_4/k_2 for styrene inhibition and log $k_4/(k_2 + k_3)$ for allyl acetate plotted against the gas-phase oxidation potential of the corresponding quinone.[12] The gas-phase values are used here since for comparison with phenomena occurring in non-polar solvents it is desirable to eliminate the solvation effects characteristic of the solvents in which potentials are determined experimentally. It is not at all surprising that the relation

[11] Breitenbach and Breitenbach, *Z. physik. Chem. A*, 1942, **190**, 361.
[12] Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 294. The potentials not reported by Conant are computed by assuming an increment of − 0·042 v. per methyl group.

between this thermodynamic property of the quinone and the fundamental kinetic quantity k_4/k_2 is not exactly linear, especially in view of the fact that some of the quinones effect inhibition by mechanisms not available to the others. In styrene the completely substituted quinones, which cannot enter into nuclear alkylation, are both weaker inhibitors than would be expected on the basis of a straight line drawn through the points for the other quinones.

The failure of benzoquinone to obey the equation based upon the simple mechanism for retardation is only one of the abnormalities distinguishing it from the substituted quinones in this study. Although the data have not proved accurate enough for a quantitative evaluation of the number of chains stopped by each quinone molecule, the whole picture is one of more benzoquinone molecules being required to stop a given number of chains than is true of the other quinones. There is evidence in the literature to support the view that benzoquinone enters into copolymerisation with styrene. From the rates and molecular weights for the thermal polymerisation of styrene determined by Suess, Pilch and Rudorfer [13] at 100°, the rate of initiation at that temperature should be equal to or less than $8{\cdot}9 \times 10^{-8}$ equivalents/kg./hr. At this same temperature Goldfinger, Skeist, and Mark [14] found that $9{\cdot}8 \times 10^{-4}$ moles/kg./hr. of benzoquinone was consumed during the induction period in the thermal polymerisation of styrene. This would correspond to at least 11 molecules of quinone being consumed for each growing chain initiated at 100°. This phenomenon does not appear to be observed at 64° where Cohen's experiments were done, and at 80°, the temperature of our experiments with allyl acetate, the amount of quinone consumed is much less. It is likely, therefore, that the free radical formed when benzoquinone attacks a growing polymer radical is just on the borderline of the stability necessary to break off the polymerisation chain, but is capable of continuing it by a reaction whose activation energy is higher than that of the usual step B in the inhibition process. This warns us not to use the inhibitor method of determining the rate of chain initiation in polymerisation at temperatures higher than those at which the method has been shown valid. Reasons for expecting benzoquinone to be possibly capable of selective copolymerisation have been given previously.[15]

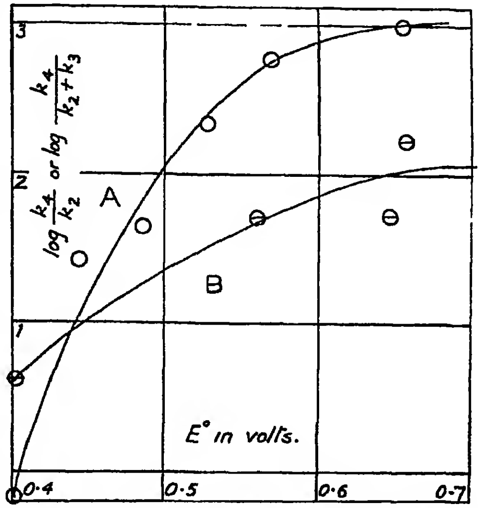

FIG. 3.—Relation between inhibitory power and oxidation potential of quinones.

A—in styrene, $\log \frac{k_4}{k_2}$.

B—in allyl acetate, $\log \frac{k_4}{k_2 + k_3}$.

Retardation of Vinyl Acetate Polymerisation by Duroquinone.—The application of a sensitive method of following polymerisation to the quinone-retarded polymerisation of vinyl acetate yields a detailed and accurate picture of the course of the reaction from the beginning through

[13] Suess, Pilch and Rudorfer, *Z. physik. Chem. A*, 1937, 179, 361.
[14] Goldfinger, Skeist and Mark, *J. Physic. Chem.*, 1943, 47, 578.
[15] Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1946, 68, 1503.

the gradual disappearance of the retarder to the point where polymerisation is proceeding at a normal rate. The method chosen was dilatometry, the sample and dilatometer being kept immersed in a thermostat at 45° throughout the run. Only duroquinone was studied in this way, its retarding action being of the right magnitude to show the nature of the reaction in the absence of sharp inhibition. From 40 to 80 points per run were taken, yielding sufficient accuracy to determine slopes reliably. Since this method of following the reaction did not permit the simultaneous determination of the initiator and retarder, their concentrations were determined indirectly by taking advantage of the following kinetic analysis, based upon the reaction scheme:

$$P \xrightarrow{k_1} 2R \text{ (initiation)}$$
$$R + M \xrightarrow{k_2} R \text{ (propagation)}$$
$$R + R \xrightarrow{k_3} X \text{ (termination)}$$
$$R + I \xrightarrow{k_4} Y \text{ (retardation).}$$

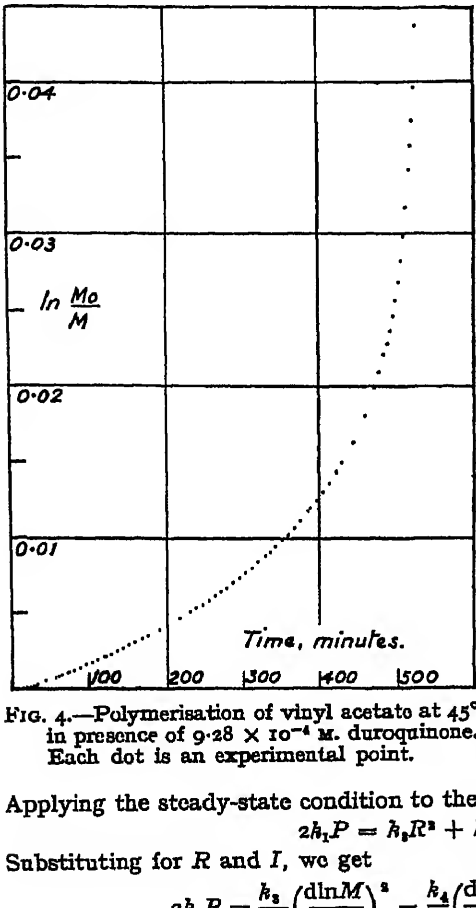

FIG. 4.—Polymerisation of vinyl acetate at 45° in presence of 9·28 × 10⁻⁴ M. duroquinone. Each dot is an experimental point.

The mechanism in vinyl acetate differs from that in allyl acetate only in the terminating step, which here consists of the interaction of two free radicals instead of the reaction of one radical with a monomer molecule.

Since $$\frac{-\mathrm{d}M}{\mathrm{d}t} = k_2 MR,$$

$$R = \frac{-1}{k_2}\frac{\mathrm{d}\ln M}{\mathrm{d}t}.$$

Since $$\frac{-\mathrm{d}I}{\mathrm{d}t} = k_4 RI,$$

$$I = I_0 e^{k_4\int R\mathrm{d}t}$$
$$= I_0 e^{-\frac{k_4}{k_2}\ln\frac{M}{M}}.$$

Applying the steady-state condition to the retarded polymerisation:

$$2k_1P = k_3R^2 + k_4RI.$$

Substituting for R and I, we get

$$2k_1P = \frac{k_3}{k_2^2}\left(\frac{\mathrm{d}\ln M}{\mathrm{d}t}\right)^2 - \frac{k_4}{k_2}\left(\frac{\mathrm{d}\ln M}{\mathrm{d}t}\right) I_0 e^{k_4/k_2 \ln M/M_0}.$$

Until quite late in a polymerisation, the retarder is accounting for such a majority of the chain terminations that the first term on the right of this equation can be safely neglected. In work to be reported elsewhere k_1 has been determined to be $1{\cdot}43 \times 10^{-5}$ min.$^{-1}$, and this constant may be used to calculate the values of P at different times. By solution of the simplified equation by successive approximations, therefore, values of k_4/k_2 can be determined as accurately as the values of $(\mathrm{d}\ln M/\mathrm{d}t)$ are obtained from the graphs. Fig. 4 shows a typical curve of $\ln M_0/M$—t. Application of the equation to points of different slope throughout the region where the curvature is maintained yields values of k_4/k_2 which are all within 10 % of 95. This tends to confirm the mechanism assumed and

the method of calculation. Duroquinone is more than 20 times as effective an inhibitor of the polymerisation of vinyl acetate as of allyl acetate.

Experimental.

Purification of Materials.—Allyl acetate was prepared by the esterification of allyl alcohol with acetic anhydride with sulphuric acid as a catalyst. After washing and drying the product was distilled through a 50-plate Lecky-Ewell column at 50-1 reflux ratio. Material boiling at 103·7° (uncorr.) with refractive index $n_D^{25} = 1{\cdot}4021 \pm 0{\cdot}0001$ was used in polymerisation experiments.

Vinyl acetate was prepared as described by Nozaki and Bartlett for their best sample. (Method D).[16]

Benzoyl peroxide, Eastman Kodak Co., was recrystallised by pouring a filtered chloroform solution into ligroin or methanol. The product was filtered and dried *in vacuo*. When stored at room temperature in brown glass the peroxide maintained its iodometric titre of 100·0 % indefinitely.

Benzoquinone, Eastman Kodak Co., was sublimed at atmospheric pressure, m.p. 115-116°.

Chloranil, Eastman Kodak Co., was recrystallised from 95 % ethanol, m.p. 288-90°. Trichloroquinone was prepared by the method of Levy and Schulz.[17] The crude product was recrystallised three times from absolute ethanol and each time the first two-thirds of the crystals deposited were discarded. The material used melted at 270·0-272·5°.

Duroquinone was prepared from durene by the method of Organic Syntheses.[18] The crude product was sublimed at atmospheric pressure, m.p. 109·0-109·5°.

Preparation of Samples.—Solutions of benzoquinone or duroquinone, peroxide and allyl acetate were made up by weight immediately before each run was started. Samples were then transferred to constricted test-tubes which had been carefully cleaned and dried. The tubes were cooled to − 80°, evacuated to 1-2 mm., closed off from the pump and allowed to warm up to room temperature and establish liquid-vapour equilibrium. The whole procedure was repeated four times and the tubes were cooled, evacuated and sealed off. After being warmed to room temperature they were placed in an oil thermostat in which the temperature was maintained constant to ± 0·01° in the work with allyl acetate and ± 0·001° in the work with vinyl acetate. Samples were removed at intervals and chilled immediately with "dry ice." In the runs with chloranil and trichloroquinone individual samples of the quinone were weighed into the tubes and the appropriate volumes of peroxide-allyl acetate solution were added by means of a volumetric pipette. After the effect of light on quinone solutions was discovered all solutions were mixed in a Corning Low Actinic flask and the runs were carried out in tubes of the same glassware except where otherwise noted.

Deterioration of Benzoquinone Solutions.—A solution of benzoquinone and benzoyl peroxide in allyl acetate was made up by weight and allowed to stand exposed to sunlight in a Pyrex flask on the laboratory desk. Samples were removed and analysed periodically. A similar solution stored in a Corning Low Actinic flask showed no deterioration. The accompanying table summarises the results.

TABLE III.—SOLUTION STANDING IN PYREX FLASK.

Time in hr.	Peroxide Moles/kg.	Quinone Moles/kg.	Allyl Acetate Moles/kg.
0·0	0·257	0·257	9·09
5·0	0·242	0·242	9·04
48	0·245	0·208	9·08
54	0·251	0·209	9·10
96	0·238	0·168	9·13
SOLUTION STANDING IN LOW ACTINIC FLASK.			
0·0	0·257	0·257	9·09
50	0·261	0·257	9·09

[16] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, 68, 2378.

[17] Levy and Schulz, *Annalen*, 1881, 210, 153.

[18] Gilman and Blatt, *Organic Synthesis*, (Wiley and Sons, New York, 1943), Vol. II, p. 254.

Absorption Spectra were determined with a Beckman Spectrophotometer, Model DU. The measurements were made in a solvent consisting of ethanol distilled over sodium hydroxide and a small amount of chloroform which was added to keep the polymer in solution. The comparison solution contained the same weight fraction of chloroform.

Conclusion.

The study of the inhibition and retardation of polymerisation of allyl acetate and vinyl acetate by quinones has shown that no single simple mechanism yet suggested for the succession of inhibition steps will account for the facts. The continuous absorption in the visible and near ultra-violet shown by the products from benzoquinone inhibition suggests a mixture containing substituted quinones and hydroquinone ethers, but which must also contain a still greater variety of coloured products, probably including polyquinone-like substances. There is chemical evidence of C— and O—alkylation of the quinone. The strongest and weakest retarders among the quinones studied were tetra-substituted compounds. Except for benzoquinone, which probably copolymerises to some extent, the quinones show the expected linear relation between log M and log I, which permits the determination of the ratio between the rate constants for inhibition and for chain propagation. The logarithms of these ratios run parallel to the oxidation potentials of the quinones, but are not a linear function of the potentials. The values of k_4/k_2 for the same retarder vary with different monomers, but not always in the direction of stronger inhibition of the less readily polymerised monomers.

Résumé.

Une étude sur l'inhibition et le retard de la polymérisation des acétates d'allyle et de vinyle par les quinones a montré qu'un seul mécanisme simple ne peut rendre compte de la succession des étapes dans l'inhibition. Les quinones, benzoquinone exceptée, présentent la relation linéaire entre log M et log I d'après laquelle le rapport des constantes de vitesse pour l'inhibition et pour la propagation de la chaîne peut être déterminé. Le logarithme de ce rapport suit parallèlementl es potentiels d'oxydation des quinones.

Zusammenfassung.

Eine Untersuchung der Unterbrechung und Verzögerung der Polymerisation von Allyl- und Vinylacetat durch Chinone zeigt, dass kein einfacher Mechanismus allein die Aufeinanderfolge der Verzögerungsstufen erklären kann. Die Chinone, mit Ausnahme von Benzochinon, geben eine lineare Beziehung zwischen log M und log I, woraus der Quotient der Geschwindigkeitskonstanten für Unterbrechung und Kettenfortpflanzung bestimmt werden kann. Der Logarithmus dieses Quotienten verläuft parallel zu den Oxydationspotentialen der Chinone.

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REACTIVITY AND STRUCTURE OF DIENES AND THEIR POLYMERS.*

PART I: REACTIVITY OF π-COMPLEX COMPOUNDS.

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Reactions involving the carbon-carbon double bond fall into two typical groups: [1] (*a*) those taking place through a free-radical mechanism and (*b*) ionic reactions. It is the purpose of the present paper to draw attention to a large group of reactions, which have in common the intermediate formation of a labile complex compound, while they may belong to either of the above groups or form a border-line case. The kinetic proof of the existence of these reactive intermediates is the occurrence of a *two-stage process*. We shall name these compounds π-complexes, for reasons which will become clear immediately, and we shall differentiate them from a transition state in that their half-life must be much longer than that of free radicals, such as $CH_3\cdot$, $C_6H_5\cdot$ or $H\cdot$, in solution.[2]

We shall proceed by giving a more detailed definition of π-complex compounds. The following sections will deal first with kinetic evidence of the occurrence of π-complexes and then with an equilibrium study of labile, but non-reactive, π-complexes. We shall finally treat the similarity existing between stabilised radicals in solution and "free atoms" of heavy elements.

Although the occurrence of π-complex compounds is a general phenomenon not related in a particular way to polymer chemistry, it is thought essential to explain their properties before dealing, in Part II of this paper, with more specialised results in the latter field.

I. The Structure of π-complex Compounds.

Dewar [3] has postulated the existence of a chemical bond between the π-electrons of an unsaturated system and an acceptor molecule or ion. It differs from an ordinary chemical bond in that it combines groups and not atoms. Dewar then postulates that the strength of this bond varies inversely with the stability of the ion, which takes part in the formation of this bond. To illustrate what is meant by this we shall repeat the examples of the upper and lower limit of π-bonds as envisaged by Dewar: (*a*) in a benzene solution of iodine the weak bond reveals its existence by anomalous colour and dipole moment, (*b*) in aromatic intramolecular-rearrangement reactions the intermediate occurrence of a very unstable OH^+ ion attached by a *strong* π-bond to the negatively charged aromatic nucleus, is made plausible on kinetic reasoning.

So far the new definition does not offer any *practical* advantage, the first case being identical with van der Waals forces, while the second case cannot be separated experimentally from a transition state. The usefulness of the conception of dative bonds from π-electrons becomes

* Communication No. 76 from the Rubber Foundation.

[1] Price, *Mechanisms of Reactions at Carbon-Carbon Double Bonds* (Interscience Publ., New York, 1946).

[2] Waters, *The Chemistry of Free Radicals* (Oxford, 1946).

[3] Dewar, *J. Chem. Soc.*, 1946, 406.

apparent in the suggestions made by Walsh,[4] who compares the similarity between

$$\begin{array}{ccc} CH_2{=\!=}CH_2 & CH_2{=\!=}CH_2 & CH_2{=\!=}CH_2 \\ \downarrow & \downarrow & \downarrow \\ Ag^+ & Br^+ & O \\ (I) & (II) & (III) \end{array}$$

where (I) represents a non-reactive, but loosely bound, π-complex, (II) a very reactive transition state (a hypothesis of long standing in the theory of bromination), and (III) is a new symbol for ethylene oxide to indicate the similarity in atomic orbitals between a 3-ring and an ethylene group. Although formula (III) has been criticised [5] we shall make use of (I)-(III) to describe here a series of complex-compounds with *gradually* changing properties.

The heat of formation of (I) has been interpreted as resonance energy [6] and we shall give further experimental evidence in support of this assumption (see section III). While these loose π-bonds with either Ag^+ or Cu^+ seem not to catalyse reactions, the introduction of Hg^{++} in the complex (I) leads to a different situation. The stability of $C_2H_4 \rightarrow Hg^{++}$ seems not to differ [7] essentially from (I) but mercuration of the olefin occurs [7] simultaneously. Substitution of ethylene by acetylene in (I) does not alter the tendency to form $C_2H_2 \rightarrow Hg^{++}$; however, a hydration of acetylene, catalysed also by a mercuri-compound but different in structure from the stable complex,[8] becomes the main reaction. This striking changes from inert silver- to very reactive mercuri-complex compounds can be better understood from the experimental details of bromination. Double bonds with a low concentration of available π-electrons show little tendency to add bromine, if, however, bromine is *first* transformed in the complex compound mercurisulphate-bromine, the reaction proceeds very fast.[9] This is clearly a two-stage process in which the first phase, the formation of the complex olefin mercurisulphate-bromine can be experimentally separated from the second step. It is of importance for an understanding of the kinetic phenomena, which we wish to discuss, to analyse the structure of this complex in more detail. We can distinguish three equilibria:

(*a*) Olefin $+ Hg^{++}SO_4^{--} \rightleftharpoons$ olefin $\rightarrow Hg^{++}SO_4^{--}$.

The π-electrons in this complex become delocalised by resonance energy.

(*b*) $HgSO_4$ aq $+ Br_2 \rightleftharpoons HgSO_4$ aq Br_2.

A very loose "association" between the mercuri-salt and bromine takes place.

$$(c)\quad \text{olefin} \rightarrow HgSO_4Br_2aq \begin{array}{l} \rightleftharpoons \text{olefin} \rightarrow Hg^{++}SO_4^{--} \\ \rightleftharpoons HgSO_4Br_2aq. \end{array}$$

The reactive labile complex is finally formed from the two primary complexes.

The second stage, i.e. the reaction, could be formally described as the simultaneous occurrence of structures (I) and (II) in the complex. But an explanation has still to be given of the part taken by the heavy Hg atom in this transformation. Some guidance can be obtained from the fact that a similarity exists between this reagent and other carriers of reactive bromine: the Hg complex causes not only addition, but also substitution.[9] The same feature has been noted [10] with IBr, while ICl

[4] Walsh, *Nature*, 1947, **159**, 165, 712.
[5] Robinson, *ibid*, 1947, **159**, 401.
[6] Winstein and Lucas, *J. Amer. Chem. Soc.*, 1938, **60**, 836.
[7] Lucas, Hepner and Winstein, *ibid.*, 1939, **61**, 3102.
[8] Frieman, Kennedy and Lucas, *ibid.*, 1937, **59**, 722.
[9] Lucas and Pressman, *Ind. Eng. Chem. Anal.*, 1938, **10**, 140.
[10] Tuot, *Bull. Soc. Chim., France*, 1942, **9**, 899.

has more tendency to substitute branched olefins [11] than Br_2. The influence of these heavy atoms then seems to favour the intermediate formation of Br radicals simultaneously with that of Br^+ ions. Another parallel can be noted between these phenomena and the versatility of "positive bromine" compounds. Bromo-succinimide, originally introduced [12] as a source of Br radicals causing substitution, forms also a molecular complex with Friedel-Crafts' catalysts and this complex produces reaction with the aromatic double bond.[13]

The last-mentioned experiment gives the close kinetic correlation between complex formation in bromination and Friedel-Crafts' catalysis. There we have to deal with an equilibrium between the three types of complex compounds, olefin-catalyst, organic halide-catalyst and olefin-organic halide. The fact then that the activity of the same catalysts depends greatly on the type of reaction [14] will be related not only to the second stage governing the formation of a new bond, but to the heat of formation of the complex compound. The latter is accessible to experimental investigation.

II. π-Complex Equilibria as a Rate-determining Factor.

Let q be the heat released in the formation of a π-complex and E the heat of activation necessary to cause reaction in the second stage, it is evident that the temperature coefficient of the overall reaction will depend on the difference between q and E. In addition, in all cases where q is small, dilution will favour the reversion of the π-complex in its components and cause an exceptional retardation of the reaction. Therefore in reactions involving loose π-bonds we may expect to observe either a marked increase of the rate on cooling to very low temperatures or a "ceiling temperature" on warming to an upper, limiting temperature at which the complex can no longer exist, and moreover, as already mentioned, an anomalous retardation on dilution. The other extreme case discussed already by Dewar, would be the formation of the unstable ion OH^+ which forms a very stable π-bond and can therefore not be distinguished kinetically from a first-order rearrangement. The experimental evidence obtainable up to now is based on incidental observations mentioned in the literature or from these laboratories. The following may serve to illustrate the occurrence of the expected phenomena.

Traces of water determine the rate of ICl formation in solution. As the reaction is accelerated by cooling, the formation of a labile hydrate $Cl_2 . (H_2O)_n$, taking part in the reaction, has been suggested.[15] ICl itself can produce not only Cl in substitution reactions, but it can also cause preferential addition of 2 mol. Cl_2 to two of the three double bonds in oleo-stearic acid.[16]

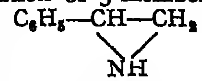
The bromine derivative of allyl chloride is formed readily from the components in high concentration but during titration in dilute solution bromine adds very slowly to the allylic double bond. Methallyl chloride, with a higher concentration of available π-electrons does not show this anomalous influence of concentration. The phenomena has been observed also with allyl chlorides of a more complicated structure. It suggests the occurrence of $(Br_2)_n$-complex compounds in concentrated solutions, from which Br^+ is easier formed than from a Br_2 molecule in dilute solutions.

[11] Bloomfield, *J. Soc. Chem. Ind.*, 1945, **64**, 274.
[12] Ziegler *et al.*, *Annalen*, 1942, **551**, 80.
[13] Schmid, *Helv. Chim. Acta.*, 1946, **29**, 1144.
[14] Price, *Organic Reactions*, Vol. III (Wiley, New York, 1946).
[15] Hildebrand, *J. Amer. Chem. Soc.*, 1946, **68**, 916.
[16] Wan and Hio, *ibid.*, 1939, **61**, 2277.

The complex formation of HCl with olefins has been suggested as a precursor to the addition reaction. That this is correct can be deduced from the explosive violence of the reaction with liquid hydrogen chloride;[17] moreover, the temperature coefficient is anomalous.[18]

The addition of HCl to isoprene was believed to lead to the 1 : 4-product only.[19] It has been shown, however, that isoprene reacts first as a non-conjugated diene because the 1 : 2-addition product is produced first, which isomerises under the influence of traces of acid.[20]

The copolymerisation of olefins with SO_2 is a radical-catalysed chain reaction. It is terminated[21] however at an upper "ceiling temperature". As the same phenomenon has been observed by Dr. G. J. van Amerongen in this laboratory in the reaction between SO_2 and olefinic polymers the inference is that a labile complex, which dissociates at higher temperatures, is a rate-determining intermediate.

The molecular weight of poly*iso*butene decreases rapidly, as is well known, with increasing temperature of polymerisation. The tentative assumption can be made that the chain-propagating step involves a complex compound, which dissociates more frequently with increasing temperature. Closely related to these reactions is the polymerisation of 3-membered imines. It has been observed that styrene-imine  is fairly stable but polymerises on the addition of acids or bases.[22] This indicates that a compound of type (III) becomes as reactive as type (II) by a change of *p*H only. More detailed studies on the properties of ethylene imine[23] reveal that violent polymerisation can be induced alternatively by Friedel-Crafts' catalysts, radicals, or a change in *p*H alone.

III. Formation and Properties of Non-reactive π-Complex Compounds.

Available information[6] combined with recent results allows one to draw some conclusions regarding the structure, strength of bond and reactivity of complex compounds with Ag^+.

INFLUENCE OF STRUCTURE.—Winstein and Lucas studied the equilibrium:

CCl_4	Water
Olefin	Olefin
	N. $AgNO_3$.

From a comparison of equilibrium constants the impression was gained[6] that steric factors overshadow the influence of available π-electrons. Bulky methyl groups surrounding the double bond cause a shift of the equilibrium to the left. We can confirm these conclusions from a study made on olefinic polymers in the equilibrium:

dioxane	dioxane
water	water
$AgNO_3$	$AgNO_3$
	polymer.

Methyl rubber with two methyl groups on the double bond shows much less affinity to silver nitrate than any other polymeric olefin. While this surprisingly large influence of two methyl groups on the double bond may be either due to hyperconjugations, i.e. a reduction of the available π-electron concentration, or to a screening effect, the preponderance of

[17] A.P. 1, 980, 396 to E. Gebauer-Fuelnegg, E. W. Mofett and Marbon Co.
[18] Mayo and Katz, *Abstr.*, 109th meeting, A.C.S., 1946.
[19] Jones and Chorley, *J. Chem. Soc.*, 1946, 832.
[20] Ultée, *ibid.*, (in press).
[21] Snow and Frey, *J. Amer. Chem. Soc.*, 1943, 65, 2417.
[22] Freundlich and Salomon, *Z. physik. Chem. A*, 1933, 166, 161.
[23] Jones, *et al.*, *J. Org. Chem.*, 1944, 9, 125, 484.

geometrical symmetry becomes more evident from a study of the solid complex compounds. We have found that a crystalline solid with a typical X-ray diagram can be produced from all olefins, the m.p. of which is roughly 120° higher than that of the olefin. No indications have been obtained for a preference to form a complex with a 1 : 1 composition.

The behaviour of polymers gives further support to the conclusion that crystallisation essentially depends on geometric symmetry. The complex compounds from synthetic polymers are amorphous while those from natural rubber [24] and gutta-percha give well-defined crystal diagrams. It was in fact this curious phenomenon which induced us to further research.

STRUCTURE AND REACTIVITY.—The properties of a complex compound necessary for a reaction are not yet fully understood. Originally it was thought that, because the ethylene bromonium ion intermediate (II) is very reactive, the analogous silver ion (I) would induce opening of the double bond, followed by isomerisation. *Cis*- and *trans*-butene have been dissolved in silver nitrate solution,[25] but no indication was obtained of partial isomerisation. The crystallisation of gutta (*trans*) and rubber (*cis*) is a very sensitive measure of the retention of the original configuration, nevertheless, no change has been observed after recovery of the polymer from the complex compounds. This result is, at first sight, rather unexpected but the cause, stabilisation of the complex by resonance, can be visibly demonstrated with dienes.

We have found, that conjugated dienes dissolve in 4 N., or saturated, aqueous $AgNO_3$ solution to give a light yellow colour. This appearance of a yellow colour means that *the degree of delocalisation of π-electrons in the diene π-complex is comparable to the state of resonance in polyenes.*

Another factor which needs further investigation is the part taken by the NO_3^- in these complexes. As aqueous solutions of $AgClO_4$ behave similarly, the contribution of the anion seems not to be of fundamental significance. However, it is known that $AgClO_4$ " dissolves " in benzene and this indicates individual differences. While the yellow crystals from dienes with $AgNO_3$ possess no greater stability than those from olefins of comparable melting point, CuCl exhibits other properties. Here the complex compound with dienes is frequently a solid which allows the separation of it from olefins. The analogy between the $AgNO_3$ complexes and aromatic complexes has been noted already from the incidence of a visible change in colour. It may be mentioned that in the latter group geometrical factors have also been found essential for the stability of the complex.[26]

IV. Some General Conclusions.

We have stated in the beginning that reactions involving π-complex compounds can be found also in reactions involving free radicals. We shall proceed now to provide arguments for this from a discussion of reactions involving (*a*) the heavy atoms, I and S, (*b*) radicals stabilised by resonance. The conclusions which can be drawn from the experimental evidence presented above can be summarised as follows.

1. Reactions of the polar type, such as the addition of halides, involve the formation of a labile intermediate as the first stage of the reaction. This first phase is frequently a true equilibrium reaction with a definite but small heat of formation, as can be deduced from kinetic evidence.

2. The forces holding these complex compounds together are of the magnitude of van der Waals forces. The olefinic part of the complex is attached to the " anorganic " fraction through the action of π-electrons while saturated molecules such as organic halides take part in the complex through the dipole interaction with the metal salt.

[24] Kratky *et al.*, *Naturwiss.*, 1938, **26**, 123.
[25] Lucas *et al.*, *J. Amer. Chem. Soc.*, 1943, **65**, 227, 230.
[26] Rapson, Saunder and Stewart, *J. Chem. Soc.*, 1946, 1110.

3. The analogy between complex compounds involving silver and divalent mercury is very close. It is therefore thought permissible to draw some general conclusions, gained from a study of the silver complex, on the nature of π-bonds in solution. Although the availability of π-electrons in the olefin is *one* essential factor determining the strength of the bond, *the other*, the screening of the double bond by bulky groups, preponderates. A differentiation between a purely geometrical influence and the reduction of π-electron concentration due to hyperconjugation cannot yet be deduced from our experiments.

One can surmise that this surprisingly powerful influence of steric factors also governs reactions involving free radicals. The preference given in studies from Kharasch's laboratory, to olefins with a terminal double bond may be taken as an indication of this.

4. Another common feature of these loose π-complexes is that the direction of the ultimate reaction can be influenced by minute changes in experimental conditions. They can be of both the radical and the polar type. The course of the reaction, and therefore the final ratio of yields, can be influenced in a reaction involving polar reagents of the Friedel-Craft type by a side reaction of the radical-type, e.g. involving oxygen; and, vice versa, the presence of Friedel-Craft catalyst can influence the course of a radical-chain reaction.

5. Obviously such a general statement as this can add nothing new in principle. Its importance has been clearly realised in silicon chemistry and in the application of labile carbonyl compounds in the addition of $CO + H_2O$ to the double bond (Reppe).

The point we wish to make clear by this discussion is that the first step in reactions involving olefins must not in general be thought of as a transition state but as a labile molecule. We shall now illustrate our line of thought by applying it to some cases important in polymer chemistry.

Reactions Involving Sulphur and Iodine.—Both these elements have in common the easy change in valency and—as a consequence of this property—the ability to form loose complex compounds in solutions and the liquid state. The concept of a "free" sulphur or iodine atom in *solution* has no physical significance. From the known properties of these elements it must be inferred that, if atoms are formed from the molecules in the dissolved or liquid state, they will surround themselves immediately, by "complex formation," with loosely bound neighbouring molecules. A "complex" of this kind may still be much more reactive than a S—S or I—I molecule but its lifetime as a radical will resemble more that of triphenylmethyl than that of phenyl.

Let us now apply point (4) of our general statement to this conception of reactive sulphur in the special case of vulcanisation. It then becomes clear that (*a*) variation of experimental conditions can easily alter the amount of crosslinking, (*b*) that a reaction involving sulphur may *simultaneously* follow a radical mechanism and be catalysed by metal salts. This argument at once removes certain difficulties [27] still present in the theory of vulcanisation.[28]

It would be expected from their position in the periodic table that the "radicals" O > S > Se > Te would lose their radical character in this order and therefore their capacity to "vulcanise" by causing crosslinking. This is borne out by experimental facts. Small quantities of oxygen always tend to cause crosslinking, while increasing quantities of sulphur have only a small influence on the degree of crosslinking.[29] Selenium alone lacks all capacity to vulcanise, but combined with sulphur, it takes part in the reaction.

The analogous line of thought can be applied to the role played by iodine in inhibition and catalysis of oxidation and polymerisation. The

[27] Naylor, *J. Polymer Sci.*, 1946, 1, 305.
[28] Farmer and Shipley, *ibid.*, 1946, 1, 293.
[29] Salomon and van Amerongen, *ibid.*, 1947, 2 (in press).

ability of iodine (and sulphur) to produce complex compounds with a half-life much longer than that of true free radicals makes their dual role in such reactions possible. Dufraisse [30] has proposed a theory of inhibition of the type:

$$A{-}O^* + \text{Inhibitor} \rightarrow A + \text{Inhibitor}{-}O^* \rightarrow \text{Inhibitor} + O_2$$

by which the inhibitor should remain active over an indefinite period While this hypothesis cannot be applied to the action of inhibitors used generally in technical polymerisation, it covers many facts known in the kinetics of reactions involving sulphur and iodine, which are difficult to reconcile with the conventional chain theory. The point which obviously needs more specification is the definition of a free radical in the liquid state which will now be discussed.

Reactions Involving Free Radicals in the Liquid State.—A stabilisation energy of about 7 kcal. on formation of triphenylmethyl can be deduced from equilibrium measurements.[31] How much of this energy can be attributed to a change in van der Waals attraction with the solvent cannot be ascertained but it seems likely that the free valency will considerably increase the tendency to form a complex with the solvent. In contrast with the non-stabilised radicals, triphenylmethyl has properties and a reactivity quite comparable to that of a complex compound. It does not induce polymerisation and adds readily to the double bond. This we find to be the case also with a number of sulphur compounds which react readily with the double bond, but do not cause crosslinking in polymers.[32] The similarity to the $R{-}CH_2{-}S$ radicals prominent for their ability to act as a chain-transfer agent, is obvious. It can be surmised that the "co-ordinative power" of sulphur in these radicals contributes to the long life or, in other words, the high stability and the tendency to add preferentially to the double bond.

In polymer chemistry, activity of a free radical can be estimated from its tendency to produce crosslinks in natural rubber. The double bond in this polymer is less readily accessible than the terminal double bonds occurring in polybutadienes. Moreover, for other reasons [33] addition of radicals to the double bond will cause cyclisation rather than vulcanisation in natural rubber. Crosslinking therefore will be due to abstraction of hydrogen in the α-methylenic position. Diazo-aminobenzene a potential source of $C_6H_5\cdot$ radicals has a much more pronounced vulcanising effect than benzoyl peroxide from which $C_6H_5COO\cdot$ radicals [34] are also formed. The borderline case can be found in a number of halides [35] which on decomposition cause crosslinking of the terminal vinyl groups in polybutadienes but do not produce the effect of vulcanisation in natural rubber.

To sum up, the kinetic characteristics of a free radical in solution are gradually changed to that of a labile complex compound with increasing stability of the radical. A radical of long-life acquires the ability to add preferentially to the double bond. The accessibility of the double bond to such a radical is *increased* by the availability of π-electrons but *decreased* by the screening effect of bulky groups surrounding the bond. The influence exerted by catalysts on reactions involving labile complex compounds or, what is the same, stabilised radicals, can be correlated with the properties of the atom. This has been suggested for the case of sulphur, iodine and related compounds; more information on the properties of atomic orbitals is, however, needed in the case of catalysis through heavy metals.

[30] Dufraisse and Chovin, *Handbuch der Katalyse*, Vol. II (Wien, 1940).
[31] Ziegler, Orth and Weber, *Annalen*, 1933, **504**, 131.
[32] Cunneen, *J. Chem. Soc.*, 1947, **37**, 135.
[33] Farmer, *Adv. Colloid Sci.*, Vol. II (Interscience Publ., New York, 1946), p. 305.
[34] (*a*) Farmer and Michael, *J. Chem. Soc.*, 1942, 513; (*b*) Hermans and van Eyk, *J. Polymer Sci.*, 1946, **1**, 407.
[35] Sturgis, Baum and Trepagnier, *Ind. Eng. Chem.*, 1947, **39**, 64.

In conclusion the author gratefully acknowledges valuable discussions with Drs. J. van Alphen and G. J. van Veersen, and thanks the Rubber Foundation for permission of publication.

Summary.

1. π-complex compounds is the name, proposed by Dewar, for labile molecules formed by the interaction of π-electrons in unsaturated systems with a second molecule or ion. It is pointed out that the intermediate occurrence of π-complex compounds, with a measurable life-time, in polar as well as radical reactions, is of great importance.

2. As the formation of an intermediate π-complex is accompanied by release of heat, it must be expected that the temperature function of the reaction and other kinetic criteria become anomalous if the complex is a rate-determining factor. Experimental evidence for this is given.

3. Factors influencing the strength of the π-bonds are evaluated from an equilibrium study on silver nitrate-olefin complex compounds. It is found that the availability of π-electrons is essential but that the "steric effect" of bulky groups can preponderate. The latter may be correlated with the first factor by hyperconjugation. The melting points of solid complex compounds depend on the same factors of geometrical symmetry as the melting points of the olefinic hydrocarbons. Solid and liquid complex compounds from conjugated dienes are light yellow, comparable to the colour of polyenes.

4. It is pointed out, that the first step in reactions involving olefins is frequently a labile molecule. A better understanding of the properties of this long-living intermediate is essential for further development in polymer chemistry. The intermediate formation of π-complexes are assumed in reactions involving sulphur and iodine. Inconsistencies in present kinetic theories can be removed by taking this into account. The concept of a free radical in solutions needs specification by a consideration of its life-time. Stabilised radicals have the kinetic characteristics of π-complex compounds. Differences in crosslinking tendencies of natural and synthetic rubbers can be explained on this assumption.

Résumé.

On souligne l'importance des composés complexes-π, qui ont une vie mesurable dans les réactions polaires et dans celles de radicaux. Les facteurs, qui influencent la force des liaisons-π, sont évalués d'après l'étude des composés nitrate d'argent-oléfine. Des contradictions, présentes dans les théories actuelles, peuvent être supprimées, si l'on suppose l'existence de tels complexes-π intermédiaires dans les réactions comportant le soufre et l'iode. Les complexes-π sont très importants dans la chimie des polymères.

Zusammenfassung.

Die Bedeutung von π-Komplexverbindung mit messbarer Lebensdauer für polare und Radikalreaktionen wird hervorgehoben. Die Faktoren, die die Stärke der π-Bindungen beeinflussen, werden durch Untersuchung der Silbernitrat-Olèfin Komplexe ausgewertet. Widersprüche in gegenwärtigen Theorien können beseitigt werden, wenn angenommen wird, dass solche Komplexe als Zwischenprodukte in Reaktionen mit Schwefel und Jod auftreten. Die Bedeutung von π-Komplexverbindungen in der Chemie der Polymeren wird erörtert.

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REACTIVITY AND STRUCTURE OF DIENES AND THEIR POLYMERS.

PART II: SYNTHETIC AND NATURAL RUBBER.*

By G. Salomon.

Received 6th August, 1947.

We have studied polymerisation reactions of dienes in order to evaluate the position of polyisoprenes within a broad range of polymers, only a small number of which is commercially available. The first section gives some aspects of polymer synthesis while in the second, correlations existing between dienes and polymer structure are discussed. The preparation of derivatives from natural rubber has been treated already by a number of authors. We shall therefore report no essentially new experimental facts, but existing kinetic correlations between dienic and olefinic reactivity will be pointed out.

The occurrence of π-complex compounds as a rate-determining step in olefinic reactions has been discussed in part I. It will be assumed throughout this paper that (*a*) the capacity to act either as a donor or an acceptor of π-electrons is essential for the course of a reaction; (*b*) a great number of radicals, particularly those involving sulphur and iodine, are stabilised in solution and therefore kinetically very similar to π-complexes.

I. Polymerisation of Dienes.

In a study of homogeneous polymerisation [1] it was found that the rate of dimerisation diminishes in the sequence: butadiene (1) > isoprene (0·6) > 2:3-dimethylbutadiene (0·3). As a consequence of this side reaction it is impossible to follow the homogeneous polymerisation of butadiene with great accuracy while methylrubber can be produced in almost quantitative yields and polyisoprene to about 92 %. It will be convenient to give first some information on catalysts.

Inhibitors and Initiators.—Introduction of inhibitors allows the study of Diels-Alder reactions without interference of a simultaneously-occurring polymerisation, while a good initiator is essential for the performance of high yields of elastomers. The three dienes show considerable tendency to polymerise under the influence of traces impurities, which are present even if particular care is taken to exclude oxygen. The efficiency of an inhibitor can be measured by the suppression of this "heat polymerisation". Nitrocompounds such as picric acid and trinitrotoluene have been found most effective with vinyl compounds,[2] and we can confirm this observation for dienes, only traces of polymers being formed after weeks at 100° C. Pyrogallol and hydroquinone are approximately equally effective, while iodine and organic iodine compounds, e.g. iodoform, show a somewhat different behaviour. They permit a certain amount (5-10 %) of polymer to be formed, but this is oily, indicating a strong chain-transfer activity. The same observation has been made for sulphur compounds such as thiophenol, while sulphur itself and thiourea produce a weak catalytic effect. The change from inhibitor to initiator is a very gradual one, comprising such different compounds as silver nitrate, acetic acid and chloranil which initiators

* Communication No. 77 from the Rubber Foundation.

[1] Koningsberger and Salomon, *J. Polymer Sci.*, 1946, 1, 200.

[2] Frank and Adams, *J. Amer. Chem. Soc.*, 1946, 68, 908.

have in common a strong tendency to reduce the size of the polymer. This is also the case with most organic peroxides, which are surprisingly weak initiators. The explanation is probably that most of the decomposition products are stabilised by resonance and show therefore little tendency to add to the diene, reacting finally with allylic hydrogen or the double bond in the polymer.

The only interesting initiator that we have found [1] is diazo-aminobenzene. As all other compounds of this group are less active it is probable that the continuous formation of phenyl radicals produces the desirable catalysis. The usual increase of the rate with the square root of initiator concentration was also found for dienes.

The influence of vinyl compounds on the rate of polymerisation is surprisingly small [3] but we have made two relevant observations in this field. Dr. van der Meer has found that isoprene is a very effective inhibitor for the polymerisation of vinylidene chloride, a result which can probably be explained by the findings from Kharasch's laboratory.[4] The second interesting point is the violent reaction of acrylic nitrile, polymerised either in bulk or in solution,[3] which is very different from that of other vinyl compounds under similar conditions. Addition of either a diene or a second vinyl compound modifies fundamentally the high activity of the acrylic nitrile radical and its true properties are therefore ill-represented by figures of relative reactivity in co-polymerisation.

The type of polymer obtained from emulsions [5] differs much less from bulk-polymers than was expected at the beginning of our research. The essential function of the emulsion seems only to be the production of more, and very reactive, radicals at lower temperatures. The fact, however, that the same type of polymer is produced 10^4-10^5 times faster, suggests that the interface has an accelerating effect which is not yet completely understood. An interesting detail in this field is the outstanding catalytic effect produced also in emulsions by diazoaminobenzene [5, 6] which is probably not due to radical formation, but to the capacity of the azo-group [7] to transfer oxygen.

Elastomers.—The rate of polymerisation is essentially the same for the three dienes, but the nature of the reaction products is very different.[1] The tendency to cross-link decreases in the series, butadiene $\gg$ isoprene $>$ dimethylbutadiene. Consequently the polybutadienes become quickly insoluble even at low yields while the products from dimethyl butadiene are soluble even at very high yield. Long reaction times in bulk or preparation in emulsion produces a moderate amount of crosslinking in the latter, which, however, can be broken down easily on the mill. This tendency to crosslink is, of course, the crucial point in the polymer chemistry of butadiene. It is obviously correlated with the fact that the $—CH_2{=}CH_2$ groups, from 1 : 2-polymerisation in butadiene are more apt to polymerise further than the $—C(CH_3){=}CH_2$ groups in dimethylbutadiene. Moreover, the occurrence of the first group in butadiene polymers is more frequent than the latter in polyisoprene and methyl-rubber.

The principal difference between vinyl polymers and polymers from dienes is the extraordinary change in physical properties of the latter as a function of yields. The "heat polymers," produced by the action of small quantities of peroxidic impurities, are rubber-like even at very low yields, but all polymers produced by the intentional addition of initiators are oils rather than rubbers at very low yields, and their hardness and "snappiness" grows gradually with higher yields. They pass through

[3] Koningsberger and Salomon, *J. Polymer Sci.*, 1946, 1, 353.
[4] Kharasch, Reinmuth and Urry, *J. Amer. Chem. Soc.*, 1947, 69, 1106; see [3].
[5] Salomon and Koningsberger, *J. Polymer Sci.*, 1946, 1, 364.
[6] Berezan, Dobromysla and Dogadkin, *Bull. Acad. Sci. U.S.S.R.*, 1936, 409.
[7] Garvey, Jr., Fryling and Semon, U.S. Pat. 2,376,963; 2,375,987; 2,376,014.

a maximum of rubber-like properties, which is near 60-70 % yield for butadiene but above 90 % yield for isoprene and can be observed only on prolonged heating in the case of dimethyl butadiene. As a consequence of these consecutive reactions, synthetic polymers are extraordinary inhomogeneous in size, this is sometimes not fully appreciated as the formation of a large "gel-fraction" tends to obscure the fact at higher yields.

One obvious result of co-polymerisation is the reduction of crosslinking, the polybutadienes are thus shifted into the region of technologically-useful rubbers. As is well known, the maximum of mechanical quality at about 70 % yield is observed also in co-polymerisation of butadiene, while it occurs for systems based on isoprene or dimethyl butadiene at higher yields.

Diels-Alder Reactions.—As already mentioned this side reaction interferes with polymerisation. It is of particular interest as a relative measure of the acceptor properties of the double bond. Taking isoprene as a standard donor under antioxidation conditions we can roughly distinguish the following changes in acceptor properties.

1. Maleic anhydride, maleic imide, azodicarbonic acid esters and SO_2 react rapidly at room temperature. As is well known, substitution of the two hydrogen atoms in maleic anhydride by methyl groups, destroys the dienophilic properties and this is a strong support for the assumption that lack of π-electrons on the double bond are the essential factor in determining dienophilic properties.

2. A slow reaction at 70° C. and a fast reaction at 100° C. has been found for esters of acetylene dicarbonic acid, acrolein and acrylic nitrile. The ethylene compounds of this class have, in common with the first-mentioned, an overall shortage of π-electrons, but has not the symmetry of charge distribution occurring in the first group.

3. A slow reaction at 100° C. and a moderate reaction at 125° C. has been observed for a great number of compounds, e.g. ester of maleic acid and acrylic acid, methylacrylonitrile, styrene and so on. Their acceptor properties become similar to those of the double bond in isoprene.

4. The rate of dimerisation of isoprene has a half-time of 240 hr. at 100° C., 36 hr. at 125° C. and 7 hr. at 150° C. The influence of methyl-groups on dimerisation, changing from butadiene to dimethyl butadiene, is surprisingly small (compared with the effect on maleic anhydride). This may be due to the compensation of two factors. Methyl groups tend to increase the resonance in the diene and therefore the donor properties in 1 : 4-position, while they increase simultaneously the π-electron concentration on the olefinic-(acceptor-) double bond, thus diminishing the acceptor properties of the latter. As an olefin $R{-}C(CH_3){=}CH_2$ has not the slightest acceptor properties for dienes at the same temperature, the acceptor properties of the 1 : 2- and 3 : 4-double bond in dienes must be entirely due to resonance.

Summing up, we can state that the dienophilic properties of a double bond change gradually from maleic anhydride to the 1 : 2-group in dimethyl butadiene, the temperatures of similar reactivity being more than 100° higher in the latter case.

Depolymerisation.—The stability of the six-membered ring system produced by a Diels-Alder reaction depends essentially on the gain in resonance energy on decomposition. Adducts with maleic anhydride are therefore only moderately stable, while the terpenes produced by dimerisation of isoprene, decompose at much higher temperatures. It has been shown that under suitable experimental conditions 60 % isoprene can be obtained from dipentene.[8] The loss of 40 % is due to secondary pyrolytic reactions. It follows from theoretical considerations[9] that the

[8] Davis, Goldblatt and Palkin, *Ind. Eng. Chem.*, 1946, 38, 53.
[9] Bolland and Orr, *Trans. I. Rubber Inst.*, 1945, 21, 133.

long-chain radical produced in the pyrolysis of natural rubber should be particularly unstable, and the large gain in resonance energy should cause depolymerisation in a chain reaction leading either to dipentene or isoprene as main product. Dr. Boonstra and Dr. van Amerongen in this laboratory have produced experimental evidence for the correctness of this theory. Natural rubber can be converted to isoprene with a yield of 60 % under suitable conditions,[10] the remaining 40 % being pyrolytic by-products, similar to those formed in the decomposition of dipentene.[8]

A high yield of dienes can only be expected from a straight-chain polymer; the method can be used therefore as a relative measure for a regular chain structure. Dr. van Amerongen has found 46 % isoprene from polyisoprene and only 14 % diene from Buna S, 8 % from sodium-Buna 115. Methyl-rubber on the other hand can be converted to 58 % diene. These results are in good agreement with other evidence, indicating a more regular structure of methylrubber and a decrease in regularity from isoprene to butadiene polymers,[11] while the sodium-polymerised butadiene has a particularly high concentration of vinyl side groups.[12]

II. Structure and Mechanical Properties of Elastomers.

Comparing natural rubber with synthetics we have to distinguish between (*a*) structural factors influenced by the method of polymerisation, and (*b*) differences in properties due to the application of molecular units other than isoprene. Rubberlike elasticity is strongly dependent on temperature. It can be deduced from a number of recent investigations[13] that the "brittle point," the temperature at which the polymer becomes brittle on fast deformation, is primarily dependent on polymer structure. From an evaluation of available data[11] the following conclusions have been reached.

1. The regular sequence $—CH_2—CH{=}CH—CH_2—$ produces a very flexible polymer chain, which, in the ideal case of a pure 1 : 4-polybutadiene, has a brittle point near -100° C.

2. Insertion of $\begin{array}{c}—CH_2—CH— \\ \quad\;\; | \\ \quad\;\; R\end{array}$ groups either by co-polymerisation or by 1 : 2-addition, leads to a stiffening of the chain and therefore to a considerable increase in the limiting temperature of elasticity.

3. Introduction of one methyl group in the diene (isoprene) raises the brittle point by 40° and a second methyl group (2 : 3-dimethylbutadiene) produces a further rise of 30°, or in the case of polymethylpentadiene even 50°. This reduction in molecular mobility has also been deduced from a study of gas permeability.[14]

4. It follows from (2) and (3) that vinyl co-polymers from a methyl butadiene or a dimethylbutadiene have a brittle point far above that of natural rubber, and must therefore lose their rubber-like properties near 0° C. This has been proved[15] in the series of acrylic nitrile-diene co-polymers. They show the expected influence of the methyl group on the rate of recovery, while they do not differ in their swelling equilibria, the latter depending essentially on the nitrile concentration.

These observations lead to the following conclusions: (*a*) the number of possible rubber-like polymers derived from dienes is limited in principle by insufficient "freeze-resistance," (*b*) a very flexible chain can be only

[10] Neth. Pat. 58,427 to Boonstra, van Amerongen and Rubber Foundation.
[11] Salomon and Koningsberger, *J. Polymer Sci.* (in press).
[12] Yakubchik, Vasiliev and Zhabina, *Rubber Chem. Tech.*, 1945, 18, 780.
[13] (*a*) Boyer and Spencer, *Adv. Colloid. Sci.* (Interscience Publ. 1946), Vol. II. (*b*) Liska, *Ind. Eng. Chem.*, 1944, 36, 44. (*c*) Borders and Juve, *ibid.*, 1946, 38, 1066.
[14] van Amerongen, *J. Appl. Physics*, 1946, 17, 972.
[15] Salomon, *J. Polymer. Sci* (in press).

produced by preponderant 1 : 4-addition in the butadiene and isoprene series and not by co-polymerisation. This leads us back to the kinetic problem of 1 : 4-addition.

The inference that the tendency for 1 : 4-addition increases in the series, butadiene < isoprene < 2 : 3-dimethylbutadiene is based (*a*) on the analogous decreasing acceptor properties in the Diels-Alder reaction, (*b*) depolymerisation, (*c*) mechanical properties of the polymers.[11] The paradoxical situation thus exists, that the presence of methyl groups in dienes, while desirable from a kinetic point of view, have an unwanted effect on the elastic properties of the polymer. Polybutadiene from radical-catalysed synthesis contains 20-25 % vinyl groups,[16] which indicates a preference for 1 : 4-addition by a factor of 4-5. As this is due to the state of resonance in butadiene it is difficult to imagine that the ratio 1 : 4/1 : 2-addition could be influenced by variations in radical initiation. The metal-catalysed polymerisation on the other hand is a typical two-stage process,[17] in which the ratio 1 : 4/1 : 2-addition can be changed [13] by experimental conditions.

The high degree of symmetry in natural rubber causes a unique phenomenon. The melting-point of the crystalline fraction in stretched rubber approaches the melting-point of straight-chain paraffins. The crystals in stretched Neoprene lack this property completely and there is no satisfactory evidence for the absence of $—CCl=CH_2$ side groups in Neoprene. The synthesis of a straight-chain olefinic elastomer comparable in regularity to natural rubber has therefore not yet been performed.

III. Derivatives of Natural Rubber.

Results obtained in this laboratory during the war were not published for obvious reasons and it was found later that the experimental evidence was similar to that produced already by Farmer [18] and by Bloomfield.[19] We shall therefore summarise only some points relevant to a discussion on labile molecules.

A. General Considerations.—The great reactivity of allylic hydrogen is readily ascertained in the study of rubber derivatives, but the peculiar fact, that the secondary hydrogen in α-methylenic position exclusively and not the hydrogen atoms in the methyl group of natural rubber react, has only gradually emerged from the combined evidence produced by the B.R.P.R.A. team. Two factors can now be separated. The general properties of a tertiary olefin and the specific influence of resonance in the rubber chain.

The π-electron concentration in a tertiary double bond is high and, as a consequence, polar reagents, e.g. HCl are readily added. Radicals should also add readily to the double bond, but are found to abstract preferentially the α-methylenic hydrogen in certain cases. Which of the two alternative reactions becomes preponderant seems to depend on the nature of the radical.[20] This competition between an attack at either the α-methylenic hydrogen or at the double bond is influenced by the occurrence of hyperconjugation in polyisoprene molecules.[21] The double bond becomes stabilised by resonance and therefore less reactive. This suggestion finds support in recent results obtained by Cunneen.[22] Radicals of the " chain-transfer agent " type R.S· (see part I) add only to the double bond, but the ease of addition decreases in the order methylcyclohexene > dihydromyrcene > squalene > rubber. In the case of thioglycolic

[16] Marvel, Bailey and Inskeep, *J. Polymer Sci.*, 1946, 1, 275.
[17] Schulz, *Ber.*, 1941, 74, 1766.
[18] Farmer, *Trans. Faraday Soc.*, 1942, 38, 340.
[19] Bloomfield, *J. Chem. Soc.* 1944, 114.
[20] Bolland and Gee, *Trans. Faraday Soc.*, 1946, 42, 246.
[21] Bateman and Jeffrey, *J. Chem. Soc.*, 1945, 211 ; Bateman and Koch, *ibid.*, 1945, 216.
[22] Cunneen, *ibid.*, 1947, 134.

acid Holmberg[23] had found addition to rubber. Dr. van Melsen in this laboratory has reproduced these experiments. Cunneen, on the other hand, working with extremely pure rubber, finds no reaction at all. The inference can be made that impurities present in rubber catalyse the addition of thioglycolic acid to rubber.

B. Chlorination.—The addition of chlorine to the double bond has been performed by Bloomfield[19] (*a*) with very pure rubber and sulphuryl chloride under peroxidic conditions (Kharasch), (*b*) using phenyliodonium chloride, another example for the directing influence of iodine compounds (see part I).

The ease of reaction of silver nitrate with allylic chloride and the non-reactivity of silver nitrate with dichlorides has been used by Bloomfield to determine the above structure. Dr. Koningsberger and Dr. Ultée, in collaboration with the present writer, have made use of reactions with organic bases to develop an analogous system of kinetic analysis. Our results are in excellent agreement with the earlier findings of Bloomfield.

Chlorine in solution acts as a "hot chlorination" agent and from a combination of Bloomfield's and our test methods it followed that only secondary allylic chloride is produced. Fractionation of the rubber chloride, however, revealed that the product is very inhomogeneous. The rate of reaction is obviously so high that the reaction is controlled by the rate of diffusion on mixing the components. It was surprising therefore, that a *homogeneous* distribution of allylic chlorine in the rubber can be produced from interaction with sulphuryl chloride.[24] As this anomalous course of reaction is found only in presence of the nitrogenous impurities of natural rubber it can be deduced that a labile "positive-halogen" compound is produced first. This new catalytic decomposition of sulphuryl chloride is analogous to the known catalytic decomposition of benzoyl peroxide.

Swelling and mechanical properties of rubber-allylic chloride resemble Neoprene; while chlorine in the latter is very stable, the former is found to be extremely reactive. Crosslinking readily occurs and becomes accelerated by heating with metal oxides. In metathetic reactions the tendency to form the stabilised rubber-allyl radical is so great that it has been found impossible to produce a quantitative exchange of chlorine with other groups.

C. Reactions with Olefins.—Two types of reactions lead to a combination of olefins with rubber. The one is related to the Diels-Alder reaction and has been termed by Alder[25] "substitutional addition"; the other is of the radical-initiated type. While the acceptor properties of the double bond in the olefin determine the ease of addition to rubber in the first case, the course of the reaction in the second case is influenced by the life-time of intermediate radicals. Both factors are closely related as will be now discussed.

The addition of maleic anhydride (MA) to olefins has found practical application in the oil industry for a long time.[26] Alder and co-workers have described it in great detail[25] and Dr. J. A. van Melsen studied it in 1941 in this laboratory,[27] while Farmer[18] has first proposed the succinic anhydride structure —CH(MA)—C(CH_3)=CH—CH_2— as the result of a reaction with the α-methylenic C—H—bond. The exceptional reactivity of this group in rubber makes the formula probable although in other cases an attack on the carbon of a *terminal double* bond has been found to occur.[28] The reaction with natural rubber is fast at 150° C. while

[23] *Ber.*, 1932, 65, 1349.
[24] Neth. Pat. 59,148 to Koningsberger and Rubber Foundation.
[25] Alder, Pascher and Schmitz, *Ber.*, 1943, 76, 27.
[26] French Pat. 743,302 to N. V. Bataafsche Petroleum Mij.
[27] Neth. Pat. 59,141 to van Melsen and Rubber Foundation.
[28] Ross, Gebhart and Gerecht, *J. Amer. Chem. Soc.*, 1946, 68, 1373.

isobutene[25] reacts only at 200° c. It would be expected that other dienophilic olefins would also react with rubber. Nearest to the maleic anhydride are the maleic *N*-alkyl imides, which have been studied extensively by Delalande[29] and are capable of reacting at 130° c. We have found that esters of acetylene dicarbonic acid as well as acrolein add readily. Maleic acid and fumaric acid add slowly at 200-220° c., while styrene and other olefins, having only weak dienophilic properties, either polymerise or not add at all.

The kinetics of the reactions are frequently of a high order indicating "autocatalysis." The latter may indicate π-complex formation but can also have physical causes as the miscibility of rubber with the olefin is low and improves gradually during the formation of the derivative. Because of this complication a precise relative scale of acceptor properties cannot be drawn up similar to that of the Diels-Alder reaction with isoprene.

Another peculiarity is the tendency to form crosslinks. The adducts of maleic anhydride gradually split off CO_2 with formation of new C—C bonds and a reaction analogous to the dimerisation of succinic anhydride to the dilactone of acetonediacetic acid[30] occurs; the mechanism of this "polymerisation" is still obscure. The ready addition of azo-esters to elastomers has been described by Alder.[25] Flory[31] has recently studied this reaction in greater detail and found the dis-azo-esters to be also powerful vulcanising agents. The latter property runs parallel with their activity as initiator in polymerisation,[7] and is, in the opinion of the present writer, due to the activation of oxygen. These phenomena indicate that the borderline between "polar" addition and radical reactions is rather diffuse. This becomes particularly evident from the work of Delalande who finds that maleic imides can be attached to rubber (either thermal, or initiated by peroxides) at the same temperature.

Farmer[32] has suggested quite a different structure for the latter products, viz., formation of a six-ring involving two adjacent double bonds of the rubber. This ingenious assumption of a chain reaction *along* the rubber chain implies the continuous presence of maleic anhydride (or imide) molecules on all double bonds, i.e. π-complex compounds. The analogous formation of a 5-membered ring from SO_2 and rubber, suggested also by Farmer, finds support in the corresponding diene adducts and in the case of other ring-closure[33] reactions involving SO_2. In this case the primary formation of a π-complex follows from the "ceiling temperature" discovered by van Amerongen (see part I). Other olefins such as styrene and acrylic nitrile are weaker acceptors, therefore the π-complex with the rubber double bond is also weaker and the ease of autopolymerisation is so great that the reaction products[34] are not regularly attached to the double bond as can be concluded from their interaction with solvents. The structures obtained should closely resemble those assumed for the adducts of styrene to drying oils.[35]

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[29] Delalande, *Thesis* (Paris, 1947), *Int. Congr. Pure Appl. Chem.* (London, 1947), Abst. No. 322/11 E.
[30] Richter, *Organic Chemistry*, 3rd Ed. Vol. I, p. 552.
[31] Flory, *Abstr.*, 110th meeting A.C.S., 1946.
[32] Farmer, *Adv. Colloid. Sci.* (Interscience Publ. 1946), Vol. II.
[33] Lüttringhaus and Buchholz, *Ber.*, 1939, **72**, 2057.
[34] Compagnon and Le Bras, *Compt. rend.*, 1941, **212**, 616. Le Bras and Compagnon, *Bull. Soc. Chim. Mem.*, 1944, 553. Compagnon and Delalande, *Rev. Gén. Caout.*, 1943, **20**, 133.
[35] Hewitt and Armitage, *J. Oil Col. Chem. Ass.*, 1946, **29**, 109.

Summary.

The efficiency of inhibitors and initiators on the homogeneous polymerisation of dienes and differences in the properties of polymers from butadiene, isoprene and 2 : 3-dimethylbutadiene are pointed out. The dienophilic properties of a number of unsaturated compounds have been studied in the presence of inhibitors with isoprene as a standard. The significance of a straight-chain structure for the case of depolymerisation is discussed.

The limiting temperature of elasticity in a straight-chain polybutadiene is raised by two factors: (1) insertion of 1 : 2-addition groups or vinyl co-polymerisation and (2) by the introduction of methyl groups in the diene. As methyl groups seem to favour the tendency for 1 : 4-polymerisation they are desirable from a kinetic point of view but the resulting polymers and co-polymers lose their elastic properties at comparatively high temperatures.

Kinetic characteristics of substitution and addition reactions with natural rubber are discussed. The analogy between dienophilic properties of olefins and their controlled addition to natural rubber is pointed out.

Résumé.

On signale l'efficacité des inhibiteurs et des initiateurs dans la polymérisation homogène des diènes, ainsi que les différences dans les propriétés des polymères du butadiène, de l'isoprène et du 2-3-diméthyl-butadiène. On a étudié les propriétés diénophiles d'un certain nombre de composés non saturés, en présence d'inhibiteurs et en prenant l'isoprène comme standard. On discute l'importance d'une structure en chaîne droite pour la facilité de la dépolymérisation. La température-limite d'élasticité dans un polybutadiène en chaîne droite est élevée par deux facteurs : (1) introduction de groupes, qui présentent une addition en 1-2 ou copolymérisation vinylique et (2) introduction de groupes méthyle dans le diène. On discute les caractéristiques cinétiques des réactions de substitution et d'addition avec le caoutchouc naturel.

Zusammenfassung.

Die Wirksamkeit von Inhibitoren und Initiatoren für die homogene Polymerisation von Dienen und Unterschiede in den Eigenschaften von Polymeren aus Butadien, Isopren und 2, 3-Dimethylbutadien werden angeführt. Die dienophilischen Eigenschaften einer Anzahl von ungesättigten Verbindungen sind in der Gegenwart von Inhibitoren untersucht worden unter Verwendung von Isopren als Standard. Die Bedeutung einer geraden Kettenstruktur für die Leichtigkeit der Polymerisation wird erörtert. In einem Polybutadien mit geraden Ketten wird die Grenztemperatur für Elastizität durch zwei Faktoren erhöht: (1) Einführung von 1, 2-Additionsgruppen oder Vinylkopolymerisation und (2) Einführung von Methylgruppen in das Dien. Die kinetischen Kennzüge der Substitutions- und Additionsreaktionen von natürlichem Kautschuk werden erörtert.

Rubber Foundation,
Delft,
Holland.

GENERAL DISCUSSION.

Dr. M. J. S. Dewar (*Maidenhead*) (*partly communicated*) : The method of Burnett and Melville depends on the measurement of the small increase in rate of polymerisation due to reaction of transfer radicals with monomer. This increase will be $1/\overline{P}$ times the rate in absence of transfer, where $\overline{P}$ is the mean degree of polymerisation. Thus the method depends on the measurement of a second-order effect and it is therefore less satisfactory than that of Mayo which depends on measurement of the first-order variation in $\overline{P}$. The method of Burnett and Melville could only be applied where $\overline{P}$ is small, i.e. for solvents with a high tendency to transfer. It would appear that in their experiments $\overline{P}$ was very small indeed, ranging

from 2·5-15 in CCl_4 and 3·5-20 in $CHCl_3$. Since there are good reasons for believing that the velocity constants for propagation, transfer and termination are independent of P only when P is large, Burnett and Melville's results are of doubtful significance.

Moreover the method is evidently an insensitive one for detecting transfer. In order to demonstrate that transfer is negligible it would be necessary to establish that the rate of polymerisation is constant to the order of $1/\bar{P}_0$, where $\bar{P}_0$ is the degree of polymerisation in pure monomer, i.e. constant to $\sim 0{\cdot}1$ %. Therefore it is not legitimate to conclude from Burnett and Melville's measurements that vinyl acetate does not undergo chain transfer with ethyl acetate.

It is also extremely difficult to believe that the transfer radicals from aromatic hydrocarbons would not initiate polymerisation more readily than the CCl_3 radicals from CCl_4; particularly since Burnett and Melville's reactions were initiated by phenyl radicals from benzoyl peroxide. A more likely explanation of their results can be derived from the idea of submicroscopic phase-separation proposed elsewhere in this Discussion by Dr. Walling. Aromatic hydrocarbons are poor solvents for polyvinyl acetate; therefore in dilute hydrocarbon solutions such phase separation may occur, the catalyst remaining mainly in the solvent while the vinyl acetate clusters round the polymer. This segregation of catalyst and monomer should reduce the reaction rate as soon as some polymer has been formed.

It should be pointed out that the second method used by Burnett and Melville is essentially Mayo's. Their equation applies, however, only if transfer with monomer is inappreciable: this condition was probably not fulfilled in their case for pure monomer, judging by some unpublished work by Mr. Lewis in our laboratories. Using the notation of Bamford and Dewar,[1] the accurate relation is

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_0}\left(\frac{[\mathrm{M}]_0}{[\mathrm{M}]}\right)^{\frac{1}{2}} + \frac{k'_3}{k_2}\phi + \frac{k_3}{k_2}\left\{1 - \left(\frac{[\mathrm{M}_0]_0}{[\mathrm{M}]}\right)^{\frac{1}{2}}\right\}$$

where $[\mathrm{M}]_0$ is the molality of pure monomer.

Prof. E. Abel (*London*) (*communicated*): It is hardly possible to unravel the kinetics of polymerisation without suitable simplifications. However,

Solvent.	(M)* mol./l.	$-\frac{d(M)}{dt}\cdot 10^4$ mol./l./sec.	$-\frac{d(M)}{dt}\Big/(M)\cdot 10^5$	Average.
Chloroform	9·94	2·58	2·60	
	7·90	1·95	2·47	2·36
	5·98	1·39	2·33	
	4·08	0·93	2·28	
Carbon tetrachloride	9·97	2·24	2·24	
	7·93	1·72	2·17	2·19
	5·68	1·22	2·19	
	4·01	0·89	2·22	
Ethyl acetate	10·00	2·56	2·56	
	8·20	1·90	2·32	
	6·42	1·33	2·07	
	4·02	0·66	1·64	

M = vinyl acetate.

may I be permitted to give a short comment on this subject. It seems to me that some of the simplifications in use are not adequately covered by the experimental results. I am thinking, for instance, of the splitting

[1] This Discussion, p. 310.

of the rate coefficients for chain propagation and chain termination into the product of "two 'reactivities' representative of the two active polymers" (originating from Cuthbertson, Gee and Rideal,[2] and from Herington and Robertson,[3] or of the not-always-adequately-plausible introduction of equal rate coefficients within each group concerned.[4]

I wonder, therefore, whether the conclusions which Burnett and Melville draw from their experiments, are sufficiently substantiated. Discussing for example their Table I (see table, p. 369) we find that the (initial) rate of polymerisation of vinyl acetate in its mixture with carbon tetrachloride is practically proportional to the concentration (mol./l.) of the monomer in its total range, up to the pure component. Within a considerable range of concentration, the same is true for its mixture with chloroform. Within this range the values are almost independent of the nature of the solvent.

Are such findings adequate to grant a decisive insight into the kinetics of such extremely complicated chemical reactions as are polymerisations?

Prof. H. W. Melville and Dr. G. M. Burnett (*Aberdeen*) (*communicated*): It is difficult to see how the criticisms of Dr. Dewar and Mr. Lewis can be upheld in view of the results shown in the following table.

	Bulk Reaction.	Reaction in Solution.
Overall rate (mol./l./sec.)	$5{\cdot}5 \times 10^{-6}$	$5{\cdot}0 \times 10^{-6}$
Initiation rate (mol./l/sec)	$1{\cdot}6 \times 10^{-7}$	$6{\cdot}0 \times 10^{-8}$
k_p (l./mol./sec.)	$6{\cdot}7 \times 10^{2}$	$7{\cdot}0 \times 10^{2}$
k_t ,,	$2{\cdot}5 \times 10^{8}$	$2{\cdot}6 \times 10^{8}$
t (msec.)	51	81

In the bulk-polymerisation process the light path was 35 mm. whereas in solution it was but 8 mm., the solution being 40 % monomer in *n*-hexane. If, as was suggested, the discrepancy in the value of k_t reported by us,[5] was due to the strong absorption of the light in a narrow layer of the tube, then the results in the two columns would be expected to be different on account of (*a*) the difference in the effective concentration of the radicals and (*b*) the more dilute vinyl acetate used in the second case. That this does not occur appears to us to afford definite proof of the validity of the results. It should be noted that the chain lengths are such as to exclude the possibility of transfer to the solvent.

With regard to the use of benzoquinone in the inhibitor technique we consider that this is valid as long as the concentrations are so low as to exclude the possibility of an internal filter effect. Since, in our experiments we achieved a direct proportionality between the amount of inhibitor and the duration of the induction period, this condition appears to have been fulfilled. It is of some interest that the experiments have been repeated with the same results.[6]

In reply to Prof. Abel it is undoubtedly true that the expression $I\dot{} = \sum k_{m_s}(P_s)$ can be invalidated by a mechanism such as he proposes. On the other hand, if each activated molecule gives rise to only one inactive polymer molecule by a disproportionation termination reaction then it follows that the expression used by us is correct. That the termination is wholly of this type is shown by earlier observations.[2] We are also well aware of the fact that the reaction is, for all practical purposes, first order with respect to monomer, but such an assumption excludes

[2] *Proc. Roy. Soc., A*, 1939, **170**, 300.
[3] *Trans. Faraday Soc.*, 1942, **38**, 490.
[4] *Ibid.*, 1946, **42**, 668.
[5] Burnett and Melville, *Proc. Roy. Soc., A*, 1947, **189**, 456.
[6] Harris (private communication).

the possibility of the solvent taking part in the reaction, so that the scheme given in the paper was adopted to include this well-known effect.

Dr. Dewar has completely missed the point of our paper. The purpose of this paper was to show the wide variety of effects that may occur when vinyl acetate is polymerised in solvents. As is pointed out in the paper there are essentially two methods for measuring the value of the transfer coefficients. (a) The kinetic method which is specially applicable to solvents exhibiting high transfer coefficients and (b) the molecular-weight method, for solvents exhibiting low transfer coefficients. The solvents were purposely chosen in order to demonstrate experimentally that each can be appropriately used with this reaction. The first point is that under the conditions specified transfer with ethyl acetate is inappreciable. It will be seen from the results for benzene that the kinetic method is sufficiently sensitive to detect transfer, which fact has been confirmed by molecular-weight measurements.

As regards the experiments in chloroform and carbon tetrachloride, the method used, is in our opinion, quite satisfactory since the molecular weight of the polymer is of the order of 1200. There is no evidence that the individual velocity coefficients vary quickly with molecular size in this range. Moreover, it may be pointed out that in all those cases it is the ratio of the coefficients which enters in the rate expression and all the evidence goes to show that these ratios are independent of molecular size. The results, therefore, are of the significance attached to them in the paper.

With reference to the possibility of sub-microscopic phase separation, we would point out that in this system we have observed the "gel" effect with solvents such as *n*-hexane. The effect, however, is completely absent with the solvents mentioned in our paper. Furthermore, osmotic-pressure experiments with polyvinyl acetate dissolved in benzene and in ethyl acetate show that benzene is a good solvent for the polymer, the thermodynamic behaviour not being greatly different from that in ethyl acetate.

Dr. C. H. Bamford (*Maidenhead*) said: Our values for the velocity constants of chain transfer (with monomer) at 0° c. are given below for three monomers:

Styrene	$7 \cdot 47 \times 10^{-5}$ l. mol.$^{-1}$ sec.$^{-1}$
Methyl methacrylate . .	$6 \cdot 30 \times 10^{-4}$,,
Vinyl acetate . . .	$0 \cdot 123$,,

(see paper by Bamford and Dewar, and remarks by Mr. G. D. Lewis). For a given radical, one would expect these constants to be in the order:

methyl methacrylate > styrene > vinyl acetate.

The observed order therefore indicates the high reactivity of the vinyl acetate radical compared to the others for this type of reaction.

The same result follows from the figures quoted by Nozaki (his Table I). Employing the values of the propagation constants for styrene and vinyl acetate one obtains the following values for the transfer constants of the two monomers with toluene at 80° c.:

Styrene	$3 \cdot 2 \times 10^{-3}$ l.mol.$^{-1}$ sec.$^{-1}$.
Vinyl acetate . . .	$35 \cdot 2$,,

These appear to be the only data available at present for a quantitative comparison of the reactivities of different radicals in the chain-transfer reaction. It would obviously be of interest to extend the results to other radicals and solvents.

Prof. C. C. Price (*Notre Dame*) said: It is of some interest that the qualitative order of the stabilising influence of groups on a free radical, derived by Dr. Nozaki from the chain-transfer reaction:

$$R\cdot + H-\overset{|}{C}-X \longrightarrow RH + \cdot C-X$$

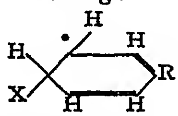
is the same as that derived from copolymerisation data, i.e., the Q constant of Alfrey and Price.

$$\text{Nozaki}: \; C_6H_5 > CH_2{=}CH > CN \cong CO_2R > Cl > CH_2R \cong OCOCH_3 > H$$
$$Q: \quad 1{\cdot}0 \quad 0{\cdot}77 \quad 0{\cdot}62 \quad 0{\cdot}55 \quad 0{\cdot}14 \quad 0{\cdot}04 \quad 0{\cdot}13$$

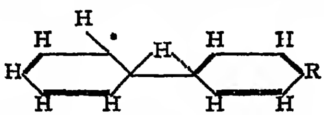
The only group out of order is the allyl group. This may be due to the fact that our Q-value is for the chloromethyl group but, from general considerations, it seems more likely that it should be placed below halogen and acetoxyl.

Dr. G. Salomon (*Delft*) (*communicated*) : It is interesting to note that the linear correlation between activation energy and frequency factor seems to be of a quite general nature. While Gregg and Mayo find new evidence (Fig. 4 of their paper) in the transfer reaction of styrene, an analogous case has been discovered by Dr. van Amerongen in this laboratory for a purely physical process, the diffusibility of gases through elastomers. Here also a decrease of E in a series of polymers is partly compensated by a simultaneous decrease in the frequency factor.

Dr. F. R. Mayo (*Passaic, N.J.*) said : I wish to suggest, as a basis for discussion, why substituted benzyl radicals and bromine atoms prefer to remove a side-chain hydrogen atom from hydrocarbons such as toluene, while a phenyl radical becomes attached to the nucleus. In the addition of any atom or radical, represented here by X, to an aromatic nucleus, the new radical will be a resonance hybrid of forms having the free valence in any one of five positions in the ring :



However, when the attacking radical is a phenyl (or other aromatic) radical, then, providing that the central hydrogen atom may be shared by both rings, several additional structures of the type



will also be available. The additional stability resulting from such structures, particularly in the activated complex, may account for the preference of an aromatic radical to become attached to another aromatic nucleus. The resulting radical would be expected ultimately to donate a hydrogen atom to some other molecule.

Prof. D. H. Hey (*London*) (*communicated*) : Dr. Mayo had focussed attention on the apparent difference in behaviour towards alkylbenzenes shown between aromatic radicals on the one hand and benzyl radicals or bromine atoms on the other hand. In the former case reaction has been reported to take place in the nucleus, in the latter cases in the side chain. I consider that it would not be profitable to discuss this question further until more experimental evidence is available. In the nuclear substitution reactions with toluene and diazotised amines, nitrosoacetanilide, and benzoyl peroxide the resulting diphenyl derivatives were usually obtained in yields of less than 50 %, and no attempt had been made to isolate and identify by-products. If any reaction had taken place at the side chain it is not certain whether the products would be benzene and dibenzyl (formed by dimerisation of two benzyl radicals) or diphenylmethane and hydrogen. Aryl radicals normally replace aromatically-bound hydrogen atoms, whereas they usually abstract and combine with aliphatically-bound hydrogen. These reactions obviously call for further investigation.

Dr. W. A. Waters (*Oxford*) said: Dr. Mayo has directed attention to the difference between free phenyl, which attacks the aromatic nucleus in toluene, and all other free atoms, or radicals, e.g. Cl•, Br•, which only attack the side-chain. This may be due to the higher reactivity of the phenyl radical, and it is important to remember that the yields in Hoy's reactions, involving $Ph^{\bullet} + C_6H_5—CH_3 \rightarrow Ph—C_6H_4—CH_3 + H^{\bullet}$ only amount to 20-50 %.

We cannot say that the reaction

$$Ph^{\bullet} + CH_3—C_6H_5 \rightarrow Ph—H + {}^{\bullet}CH_2C_6H_5$$

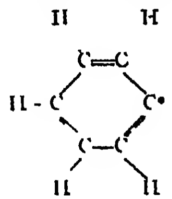
does not occur also.

Now if we look at Gregg and Mayo's chain-transfer data we see for

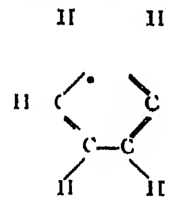
$$\begin{array}{lll} R^{\bullet} + C_6H_6 & \longrightarrow R—H + {}^{\bullet}C_6H_5 : \text{Activation energy} & E = 14{\cdot}8 \text{ kcal.} \\ R^{\bullet} + C_6H_{12} & \longrightarrow R—H + {}^{\bullet}C_6H_{11} & E = 13{\cdot}4 \text{ kcal.} \\ R^{\bullet} + CH_3—C_6H_5 & \longrightarrow R—H + {}^{\bullet}CH_2—C_6H_5 & E = 10{\cdot}1 \text{ kcal.} \end{array}$$

This indicates that the production of ${}^{\bullet}C_6H_{11}$ requires *more* activation energy than the production of a typical free alkyl radical such as cyclohexyl. It may mean that free phenyl is correspondingly a more active radical than any free alkyl.

I should be interested to learn what theoretical chemists could tell us about the structure and energy level of free aryl radicals. It is clear that ${}^{\bullet}C_6H_5$ is *not* a resonance-stabilised radical such as benzyl, because we do not change the locality of the odd electron in any of its reactions. Thus *p*-Cl—$C_6H_4^{\bullet}$ always gives us *p*-chlorophenyl derivatives, e.g. *p*-Cl—C_6H_4—C_6H_4X. The only alternative canonical structure to (I) is (II) in which we (*a*) do not have a simple conjugated system, and (*b*) have a carbon atom of " allene " type, with an impossibly-strained arrangement of its four valence bonds. Hence (II) is a state of very high energy level indeed. Even by bringing in hyperconjugation we cannot suggest



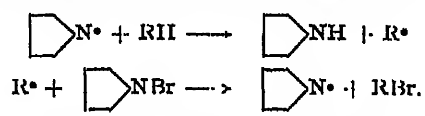
(I)



(II)

a rational alternative to (I). Dr. Mayo's remarks about resonance-stabilisation in the transition state in the attack of Ph• on benzene has important structural consequences. The transition state of any aromatic substitution process involves structures of quinonoid type in which the incoming group attacks the aromatic ring from an angle.[7] This brings the hydrogen atom at the point of nuclear attack near to the electron-system of the incoming phenyl group, and hydrogen bonding may be involved in a way which is not possible with attack of, say, atomic chlorine.

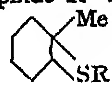
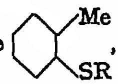
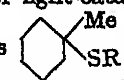
Dr. G. F. Bloomfield (*Welwyn*) (*communicated*): Dr. Salomon suggests that in substitution reactions involving bromo-succinimide, the reagent provides a source of bromine radicals causing substitution. Is it not more likely that the succinimide portion of the molecule is the effective chain carrier since chlorine radicals, and possibly also bromine radicals, tend to give additive reaction rather than substitution?



[7] Waters, *J. Chem. Soc.*, (in press).

Our application of the work of Kharasch to polyisoprenes indicates that conditions favourable to the formation of chlorine radicals lead exclusively to additive reaction of chlorine, even in systems which are preferentially substituted by chlorine itself. It is also known that bromine liberated from dimethyl sulphide dibromide Me_2SBr_2 gives exclusively additive bromination in these systems, although the exact nature of this reaction has not yet been established. Hence it seems rather unlikely that bromine radicals should lead to exclusive substitution.

It is not necessary to postulate the formation of a labile "positive halogen" compound to explain the substitutive chlorination of unpurified rubber by sulphuryl chloride, since the normal mode of reaction of sulphuryl chloride with olefins from which all peroxidic impurities are carefully excluded is mainly substitutive at 80°, while at low temperatures the reagent adds to the double bond. Additive chlorination requires both peroxidic catalysts and elevated temperatures, and it is significant that destruction of the natural inhibitors in unpurified rubber by deliberate oxidation, carried just far enough to overcome the usual induction period, enables a substantial degree of additive chlorination to be accomplished.

A reaction of sulphur compounds which may be of interest to Dr. Salomon in that it exhibits both radical and polar characteristics is the thermal reaction between polysulphides and olefins at 140-180°. Whereas addition of a radical fission product ($RS^{\bullet}$) of the polysulphide $R \cdot S_x \cdot R$ to 1-methyl-cyclohexane would be expected to give  and, ultimately, the sulphide , which is the product actually obtained from the peroxide- or light-catalysed addition of the corresponding thiol, the product found is  indicative of hydrogen capture by the $RS^{\bullet}$ radical followed by *polar* addition of the resulting thiol to the double bond.

Mr. N. Sheppard and Dr. G. B. B. M. Sutherland (*Cambridge*) (*communicated*): In Salomon's second paper he has considered the characteristics of some of the reactions of natural rubber, and his discussion raises several points of interest. We wish to comment briefly, as some results of an infra-red spectroscopic investigation throw light on the free radicals involved in certain of the reactions.

We have extended our work on the vulcanisation of rubber by sulphur,[8, 9] and in addition have investigated the products formed by the thermal degradation and chlorination of rubber. In all three cases we find that there is strong evidence for the migration of some of the double bonds in the rubber chain so that their usual trisubstituted configuration, RR′C=CHR″, becomes a disubstituted one of the type RCH=CHR′, or $RR'C{=}CH_2$. These migrations can be most easily explained by the formation, at some stage of the reaction, of free radicals, in which a hydrogen atom has been removed from one of the three carbon atoms that are in *α* positions with respect to the double bond (i.e. from carbons 1, 2, or 3 in the unit $-\underset{1}{CH_2}-\underset{2}{C(CH_3)}{=}CH-\underset{3}{CH_2}-$). Once such free radicals are formed, resonance can give final products with the double bond in the disubstituted configuration. The number and type of the disubstituted groups vary from reaction to reaction and a full description and discussion of the results will be given in forthcoming publications.

Infra-red evidence can also be used to supplement some of the other

[8] Sheppard and Sutherland, *Trans. Faraday Soc.*, 1945, **41**, 261.
[9] Sheppard and Sutherland, *J. Chem. Soc.* (in press).

points made by Salomon. Thus Harding, and Thompson [10] have investigated the structure of synthetic polyisoprenes by this means with particular emphasis on the detection of vinyl side chains. We have recently compared Harding's spectrum of a sodium-polymerised sample of polyisoprene with that of an emulsion polymerised specimen and find, in agreement with Salomon's degradation data, that the latter has largely 1 : 4 polymerised groups whereas the former consists mainly of 1 : 2 units. The question of the absence or not of $—CCl=CH_2$ groups in Neoprene has also been investigated by the infra-red method, and it has been found in the sample investigated that there is no strong absorption band in the position that would be characteristic of such a group. We conclude, therefore, that the sample of Neoprene that we examined had been formed by predominantly 1 : 4 addition of the diene units. Other features in the spectrum suggest, however, that there may be *cis*- and *trans*-type double bonds present, and these would cause irregularities in the chains.

Samples for these investigations have been supplied by the laboratories of the British Rubber Producers Research Association, and the Dunlop Rubber Co., Ltd.

Dr. M. J. S. Dewar (*Maidenhead*) (*communicated*) : The explanation of ceiling temperatures given by Dr. Salomon is pleasing but not altogether satisfactory. Thus if a reaction, $A + B + C \rightarrow$ (products) takes place through the reversible formation of an intermediate D from A and B,

$$A + B \rightleftharpoons D \quad . \quad . \quad . \quad (1)$$

$$D + C \rightarrow \text{(products)} \quad . \quad . \quad . \quad (2)$$

it should be kinetically indistinguishable from a true third-order reaction. For we shall have

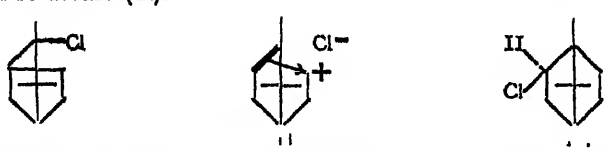
$$[D] = K_1[A][B] = e^{-\frac{\Delta G_1}{RT}}[A][B]$$

$$\frac{d\,[\text{products}]}{dt} = k_2[C][D] = \frac{kT}{h}[A][B][D]\,e^{-\frac{\Delta G_1}{RT}} \cdot e^{-\frac{\Delta G_2}{RT}}$$

where ΔG_1 is the free-energy difference in the equilibrium (1), and ΔG_2 the free energy of activation of reaction (2). The overall reaction will appear to be of third order with a free energy of activation $(\Delta G_1 + \Delta G_2)$.

The mere formation of a labile intermediate will not therefore account for ceiling temperatures. These might be explained if one component of the complex is a gas (BF_3, SO_2), or if several reactant molecules take part in the complex, but in all cases the kinetics will be indistinguishable from those of single-step reactions of higher order.

Stereochemical relations of olefine complexes certainly provide a strong argument for the π-complex theory. Another similar example is the isomerisation of camphene hydrochloride (I) to *iso*bornyl chloride (III), where no bornyl chloride is formed. This reaction, which has aroused some interest, is very easily explained if the intermediate cation has the π-complex structure (II).



Dr. G. Salomon (*Delft*) (*communicated*) : I am familiar with the fact mentioned by Dewar, that a consecutive reaction of this type is kinetically identical with a third-order reaction, but the assumption of a true three-body collision in the liquid state seems highly artificial, unless the assumption is made that the life-time of such a collision product becomes similar

[10] Thompson, *Trans. Faraday Soc.*, 1945, 41, 272.

to that of a loose complex compound. The formula used by Dewar (using the characters G_1 and G_2) is identical with the text of my paper (characters q and E). The ceiling temperature is a possible, but not necessary phenomenon, as has already been stated there. Other indications are obtained from changing the concentrations.[11]

The experiments communicated by Richards and Eley [12] seem to link the field of non-reactive complexes with the Friedel-Craft catalysts. We should like to mention in this connection, that styrene dissolved in aqueous silver nitrate is slightly yellow, quite comparable to the yellow colour of conjugated dienes in silver nitrate.

I have found that π-complex formation is a general property also of paraffinic derivatives containing groups with π-electrons or occurring in enolic form, viz.: (*a*) nitriles, (*b*) nitro-compounds, (*c*) ketones, (*d*) aldehydes, (*e*) phenols. This very large increase in solubility is not produced by other ions and is therefore a specific property of the silver atom.

The remarks of Shappard and Sutherland on the structure of Neoprene enable me to explain the following observations. All types of Neoprene react instantaneous with ICl and Br_2 to a certain percentage only (about 20-30 % with the pure polychloroprene), while the remainder of the double-bonds reacts very slowly even with a large surplus of reagent. As the infra-red evidence excludes vinyl side-groups, this must be due to a difference in reactivity between the *cis*- and *trans*-type. It is probable that the *trans*-type is more reactive with bromine. If this is the case, it would mean also that only a minor fraction of the polymer can be crystallised.

The chain mechanism for the reaction of bromo-succinimide, proposed by Bloomfield seems more likely than that suggested in my paper. I have mentioned these experiments mainly to illustrate the reactivity of a positive halogen compound in (*a*) radical initiated and (*b*) polar reactions. I think that the sulphuryl chloride reactions with olefines are more complicated than the picture given by Bloomfield; we hope to succeed in performing conclusive experiments.

Dr. F. S. Dainton and Mr. K. J. Ivin (*Cambridge*) (*communicated*): Dr. Salomon makes the suggestion that the "ceiling temperature" phenomenon in the copolymerisation of sulphur dioxide and olefines is due to the dissociation of a labile π-complex formed from the reactants. We have been working on this problem recently and the situation may not be so simple as Dr. Salomon describes. We have found that a reaction between SO_2 and hydrocarbons, both saturated and unsaturated, can be induced in the gas phase by ultra-violet light, with the formation of sulphinic acids R . SOOH, by substitution of the hydrocarbon. Let us consider the collisions of the electronically-excited sulphur dioxide molecule (SO_2*) with olefines, which lead to reaction. Firstly, if we do not assume the existence of complexes in the liquid phase, we may write:

$$SO_2^* + \underset{\displaystyle CH}{\overset{\displaystyle R}{|}}{=}CH_2 \rightarrow \cdot\underset{\displaystyle CH}{\overset{\displaystyle R}{|}}{-}CH_2{-}SO_2\cdot\ (\rightarrow\rightarrow\rightarrow \text{polymer}) \qquad (1)$$

If we assume the same reaction to occur in the gas phase, it must be followed by rapid rearrangement [13] of the diradical (I):

$$\cdot\underset{\displaystyle CH}{\overset{\displaystyle R}{|}}\,.\,CH_2{-}SO_2\cdot \rightarrow \underset{\displaystyle CH}{\overset{\displaystyle R}{|}}{=}CH{-}SOOH. \qquad (2)$$

[11] Nozaki and Ogg, Jr., *J. Amer. Chem. Soc.*, 1942, 64, 697, 704, 709.
[12] This Discussion, p. 378.
[13] See comment on Dr. Szwarc's second paper, p. 71.

Secondly, if complexes *are* assumed to exist in the liquid phase, we may write for the liquid phase reaction:

$$SO_2^* + \left\{ \begin{array}{c} \overset{\displaystyle R}{\overset{|}{C}}H{=}CH_2 \\ \overset{\nearrow S \searrow}{O \quad O} \\ \text{(II)} \end{array} \right\} \rightarrow .\,SO_2\,.\,\overset{\displaystyle R}{\overset{|}{C}}H{-}CH_2\,.\,SO_2\,.\,(\rightarrow \rightarrow \rightarrow \text{polymer}) \quad (3)$$

where (II) represents the π-complex; for the gas-phase reaction we can now write:

$$SO_2^* + \overset{\displaystyle R}{\overset{|}{C}}H{=}CH_2 \rightarrow \overset{\displaystyle R}{\overset{|}{C}}H{=}CH\,.\,SOOH \quad . \quad . \quad (4)$$

where this reaction may be strictly analogous to that occurring with a saturated hydrocarbon:

$$SO_2^* + \overset{\displaystyle R}{\overset{|}{C}}H_2{-}CH_3 \rightarrow \overset{\displaystyle R}{\overset{|}{C}}H_2{-}CH_2\,.\,SOOH. \quad . \quad . \quad (5)$$

We are now not obliged to assume the intermediate existence of the $\cdot\overset{\displaystyle R}{\overset{|}{C}}H{-}CH_2{-}SO_2\cdot$ diradical in reaction (4), though its formation is possible in view of the large amount of energy available from the excited SO_2 molecule.

Dr. Salomon has attributed the ceiling temperature phenomenon to the effect of temperature on the concentration of π-complexes (II). An alternative explanation, which does not assume the existence of such complexes, is that the effect of increasing the temperature is to reduce the stationary concentration of diradicals (I), due to the increased ease of rearrangement. The strongest argument in favour of the π-complexes is the independence of the ceiling temperature on the method of initiation and reactant ratio in the polymerisation reaction. There is, however, little independent physical evidence for the existence of π-complexes between SO_2 and olefines, and such evidence as we have obtained suggests that the equilibrium concentration of π-complexes, if they exist, is very small.

A final decision on this matter must await the results of experiments now in progress. In the meantime, it would be very interesting to know the nature of the products of the reaction between olefinic polymers and SO_2 and whether it is spontaneous or requires a catalyst.

Dr. G. Salomon (*Delft*) (*communicated*): Dainton and Ivin's results prove that, in addition to the reaction initiated by radicals studied by us, another type exists initiated by light which leads to a different reaction product.

The reaction between polymers and SO_2 is not spontaneous, but initiated by typical polymerisation catalysts. A tentative formula for the structure has been proposed by Farmer.[14]

The existence of π-complexes between SO_2 and olefins becomes evident from the solubility of olefins and aromatic compounds in SO_2, comparable to the solubility of olefins in conc. $AgNO_3$ solutions and of $AgClO_4$ in benzene (see remarks by Dewar).

The alternative assumption of the diradical (I), made by Dainton and Ivin, would need a thorough physical definition of this diradical which will encounter similar difficulties as in the case of CH_2. The final result of such considerations will probably be that the behaviour of the

[14] *Adv. Colloid Sci.*, Vol. II.

labile intermediate olefin-SO_2 corresponds under certain experimental conditions with the radical (I) and under different conditions with the π-complex (II).

Mr. Alan W. Richards and Dr. D. D. Eley (*Bristol*) (*communicated*): The observations on the association of Ag^+ with double bonds are of interest to us, since we have recently found that silver perchlorate is an active catalyst for certain polymerisations, notably of vinyl octyl ether and of styrene. We were attempting to produce I^+ ions, by the reaction of $AgClO_4$ with I_2, and thus to initiate polymerisation by I^+, when we found that $AgClO_4$ was an active catalyst in its own right. $AgClO_4$ probably falls into the class of Friedel-Crafts catalysts, since the reaction is much accelerated in solvents of high dielectric constant (cf. Dr. Pepper's results with $SnCl_4$)[15]. Dr. D. C. Pepper has pointed out to us that according to G. N. Lewis's classification of acids and bases,[16] we could expect $AgClO_4$ to be a catalyst of this type. We might suppose that the salt associates with the double bond in some way, but whether Ag^+ ion or undissociated $AgClO_4$ is concerned is not yet clear. The catalytic action of magnesium perchlorate on styrene has recently been described.[17] This substance is certainly much less active than the silver salt with the vinyl ether monomer, with which we are mainly concerned, and so we should hesitate at present to classify it also as a Friedel-Crafts catalyst.

15 Pepper, *Nature*, 1946, **158**, 789.
16 Lewis, *J. Franklin Inst.*, 1938, **226**, 293.
17 Lilley and Foster, *Nature*, 1947, **160**, 131.

C.—DEGRADATION.

THE MECHANISM OF THE THERMAL DEGRADATION OF POLYMETHYL METHACRYLATE.

By N. Grassie and H. W. Melville.

Received 16th July, 1947.

The theory of the random breaking of bonds, as put forward first by Kuhn [1] to explain hydrolytic degradation of high polymers, was insufficient to explain the thermal degradation of vinyl compounds mainly due to the large amounts of monomer which were produced even in the initial stages of the reaction. It was Simha [2] who first suggested that there was preferred breaking at the ends of the chains whereby monomeric units were produced. Blatz and Tobolsky [3] considered polymerisation and depolymerisation as a stepwise reaction and so their depolymerisation reaction was similar to Simha's preferred breaking at the ends. If we regard polymerisation as a chain reaction, however, and depolymerisation as reverse polymerisation then the degradation reaction should show totally different characteristics from either random breaking, or preferred or exclusive breaking at the ends.

The great difficulty in attempting to analyse the mechanism of depolymerisation by means of such theories has been the lack of experimental evidence based essentially on the values of the number average molecular weight determinations of the polymer residue. If conditions are sufficiently

1 Kuhn, *Ber.*, 1930, **63**, 1503. 2 Simha, *J. Appl. Physics*, 1941, **12**, 569.
3 Blatz and Tobolsky, *J. Physic. Chem.*, 1945, **49**, 77.

ideal it should be possible, by a study of the M.W. of residue — % degradation of monomer curve, to decide which is the operative mechanism. Theoretical curves for three extreme cases mentioned above are given in Fig. 1. By residue is meant all molecules present in the system other than monomer.

Obviously then, number average molecular weight determinations are of first importance in the elucidation of the fundamental nature of the reaction.

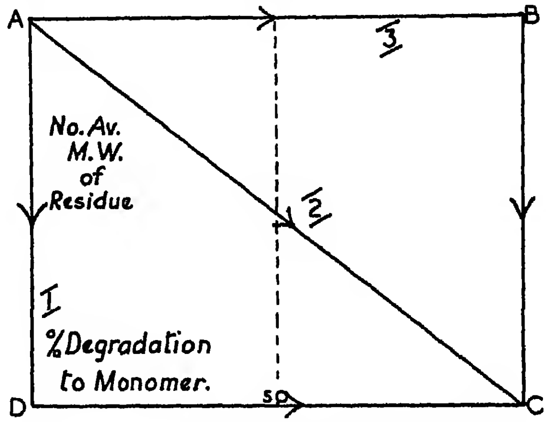


FIG. 1.—Three possible extreme degradation mechanisms.

1. Random breaking is represented by the path ADC, the molecular weight falling to a very great extent before appreciable amounts of monomer are produced.

2. Stepwise degradation is represented by AC, the fall in M.W. being proportional to the amount of monomer produced.

3. Reverse polymerisation would follow the path ABC since each molecule would disintegrate completely and the residue would have the same average molecular weight as the original.

Experimental.

Apparatus and Method.

In our experiments a new type of dynamic molecular still was used in which the pressure of air was kept down to a maximum of 10^{-4} mm. and the pressure of monomer during the reaction never exceeded 10^{-2} mm. These conditions ensured firstly, that no oxidative fission took place, and secondly, that once a monomeric molecule was produced the chances of its polymerising or taking part in any secondary reaction were reduced to negligible proportions. In this way the pure thermal degradation reaction was isolated.

The rate of degradation was found by measuring the pressure set up in the still while the monomeric vapour was being pumped out by a mercury-vapour diffusion pump pumping at constant speed. The pressure was measured by means of a Pirani gauge so that the degradation could be followed continuously. It was also possible to collect and measure the monomer produced when only the degree of degradation to monomer was required to be known and not the absolute rate.

0·2 to 0·5 g. polymer, in a finely powdered form, were degraded at a time in a small temperature-controlled copper tray which was heated electrically. Separate experiments on the addition of copper powder showed that copper has no catalytic effect. Degradation was detectable at 160° c., and 220° c. gave a suitable working rate of production of monomer.

The residue left in the tray after degradation was dissolved out with benzene and all molecular weights were determined osmotically in benzene solution by the dynamic method of Fuoss and Mead [4] with modifications due to Masson and Melville.[5, 6]

Results and Discussion.

Experiments on the fall in molecular weight with degradation were carried out on three samples of unfractionated benzoyl peroxide-catalysed polymer having molecular weights of (*a*) 179,000, (*b*) 94,000, (*c*) 36,000. The results are shown in Fig. 2.

[4] Fuoss and Mead, *J. Phyic. Chem.*, 1943, 47, 59.
[5] Masson and Melville, *Nature*, 1946, 157, 74.
[6] Masson (unpublished).

In each case there is no decrease in molecular weight in the initial stages of the reaction. Later on, however, there is a definite fall-away, but the lower the molecular weight of the original polymer, the greater the degree of degradation before this takes place, and with the 36,000 polymer the molecular weight remains unchanged until at least 65 % degradation. The form of the M.W. —% degradation curves is quite independent of the temperature at which the degradation is carried out.

These results indicate that in the initial stages of degradation of 94,000 and 179,000 polymers and for practically the whole course of the degradation of 36,000 polymer, the reaction is such that the polymer chains are split in some way, probably free radicals being formed, and once this happens the whole molecule disintegrates completely to monomer leaving no involatile residue.

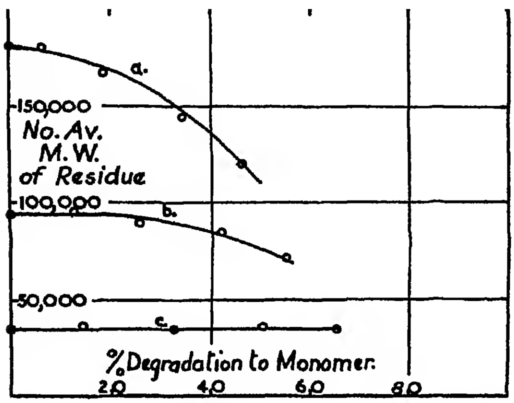


FIG. 2.—Effect of degradation on molecular weight.

If this mechanism for the reaction is correct, then it should be possible to retard or inhibit the reaction to a marked extent if a suitable agent could be found. All the usual inhibitors and retarders were useless for this particular reaction since it was essential that the required substance should be soluble in the polymer and also quite involatile and stable at 220° c. and preferably at even higher temperatures.

It was known that the leuco compound of the dyestuff 1 : 4-diamino anthraquinone gave up its hydrogen atoms fairly readily to form the dyestuff and it seemed possible that these hydrogen atoms, or the dyestuff itself, might terminate the chains before complete disintegration and so slow down or stop the reaction. An equimolecular proportion of either the dye or its leuco compound was indeed found to stop the reaction almost completely at 220° c. It was also found that, in complete absence of oxygen, the characteristic dyestuff colour was produced on warming a mixture of monomer and leuco dye. Considering the fact then, that both the leuco compound and the dye have almost the same power of inhibiting degradation, it is most probable that the leuco compound is converted to the dyestuff very early in the reaction by the first monomer produced so that its leuco hydrogen atoms never have a chance of actually terminating the chains even if it were possible for them to do so.

Both the dye and its leuco compound are quite involatile at 220° c., which was the temperature at which the experiments described above were carried out, but the dye is volatile at 280° c. Several experiments were carried out at 280° c., to find out how soon the dye was produced and it was found that all the leuco compound added to the polymer was converted to dye and evaporated off within a few seconds of the temperature reaching 280° c.

If the degradation of the polymer chains was being stopped prematurely by the action of the dye and if the polymer was being degraded by first being split into two free radicals then it should have been possible to demonstrate a relatively large fall in molecular weight in the initial stages of the degradation. Owing to the difficulty of the presence of dye molecules in the osmometer these experiments were done viscometrically in a purely qualitative way but no decrease in viscosity could be detected.

This seems to indicate that the ends of the chains are the vulnerable points at which the degradation starts, and that the dyestuff acts by blocking the ends of the chains. This, too, is supported by the fact that an equimolecular amount of dye added to the polymer is about the critical amount required to stop the degradation. The polymer was prepared by benzoyl peroxide catalysis so that one end of the chain was already blocked by either a benzoyl or a phenyl group and if it was terminated by disproportionation then only one dye molecule per polymer molecule would be required completely to stop degradation.

Measurements throughout the whole course of the reaction showed that the rate of production of monomer from polymer of different molecular weights is the same as long as the polymer has been prepared by the same general method, that is, as long as it has the same general structure.

Rate of production of monomer — % degradation curves for three samples of benzoyl peroxide polymers and one sample of pure photopolymer are shown in Fig. 3.

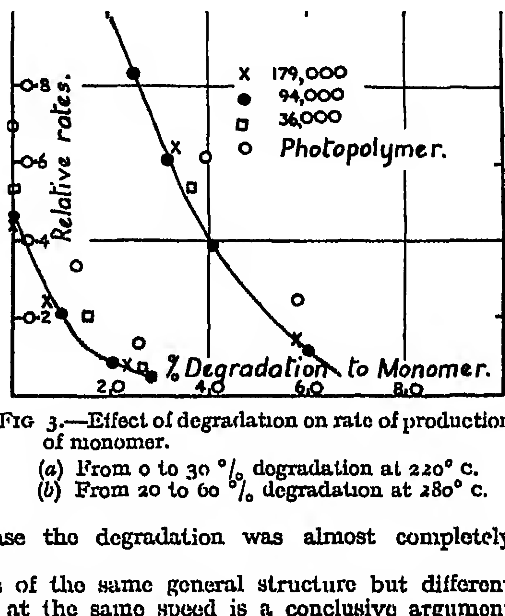


FIG 3.—Effect of degradation on rate of production of monomer.

(a) From 0 to 30 % degradation at 220° C.
(b) From 20 to 60 % degradation at 280° C.

It can be seen that the rates for 179,000 and 94,000 polymer are exactly the same and that for 36,000 polymer very close to them, while the photopolymer degrades faster. Experiments were also done with a polymer having diphenylcyanomethyl groups at both ends and in this case the degradation was almost completely stopped.

The fact that polymers of the same general structure but different molecular weights degrade at the same speed is a conclusive argument in favour of the theory of the initiation of degradation by breaking at the ends of the chains. The rate of initiation will be proportional to the number of vulnerable ends or the number of molecules, and the number of molecules in a sample is inversely proportional to the molecular weight of the sample. However, the number of monomer units obtainable from a given molecule is proportional to its molecular weight so that the rate of degradation will be the same no matter what the molecular weight may be.

The rate of degradation however, is determined by the nature of the end group on the polymer molecules because the nature of the end groups affects the rate of initiation. Photopolymer, with presumably a normal methyl methacrylate unit at each end, degrades easiest. Benzoyl peroxide-catalysed polymer degrades less easily—it has probably one phenyl or benzoyl end group and one normal methyl methacrylate end per molecule. The sample with a diphenylcyanomethyl group at each end, on the other hand degrades only very slowly.

An interesting point which arises from all this is the fact that since each molecule has the same chance of breaking then the molecular weight distribution will not change on degradation. Presumably then the 1 : 4-diamino anthraquinone inhibits the reaction due to the fact that it can block the ends of the methyl methacrylate chains by combining with

a degrading chain, which is a free radical, in much the same way as it can combine with a hydrogen atom to form the leuco compound.

The energy of activation of the reaction in its initial stages is 31,000 ± 2,000 cal. which is of the same order as that obtained by Votinov, Kobeko and Marei.[7] Their experiments were not done under molecular-still conditions but in presence of nitrogen at atmospheric pressure and their value was 25,000 cal. As degradation proceeds, however, the energy of activation increases as shown in Fig. 4.

The rate of production of monomer during degradation falls away much more quickly than is expected if it only depends upon the amount of polymer degraded. This can be explained as being due to the increase in the energy of activation and, if the rate is corrected for the decrease in the amount of polymer present and if we then calculate what it would have been if the energy of activation had remained at 31,000 cal. throughout the reaction, we find that the increase in energy of activation at least compensates for the decrease in rate. The result, however, is purely qualitative owing to the difficulty of measuring the increase in the energy of activation as accurately as would be necessary for exact quantitative agreement.

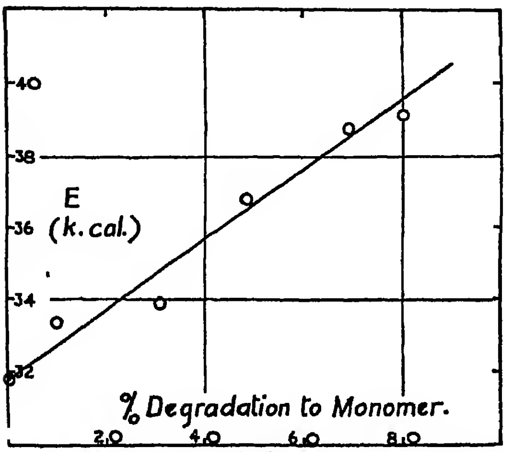


FIG. 4.—Effect of degradation on the overall energy of activation of the degradation reaction.

It has been mentioned earlier that with higher molecular weight polymers the mechanism is only strictly reverse polymerisation in the initial stages. Later in the reaction the molecular weight falls away. It is difficult to imagine any process going on from the start alongside reverse polymerisation which would have no effect in the earlier stages and which comes in to such a marked extent in the later stages. It appears, therefore, that some structure is produced thermally in the molecule, which stops the reaction before it can go to completion and this links up qualitatively with the increase in the energy of activation observed during the course of the reaction. The lower the molecular weight of the polymer too, the less chance would the molecule have of being terminated before it disintegrated completely and therefore the greater the extent of degradation before the molecular weight begins to fall away. This change in the structure of the molecule, which has been postulated to have been produced thermally and which slows down the reaction markedly, might do so in two possible ways. It may either retard the initiation step, by making some difference to the end of the molecule, or it may retard the propagation step and make it possible for the degradation to be terminated prematurely. The latter is the more probable owing to the drop in molecular weight which would not take place if only the initiation step were affected. This retarding process will have a temperature coefficient and hence produce an increase in the overall energy of activation.

Our thanks are due to I.C.I., Dyestuffs Division, Grangemouth, for samples of 1 : 4-diamino anthraquinone and its leuco compound; to

[7] Votinov, Kobeko and Marei, *J. Physic. Chem.* (*U.S.S.R.*), 1942, **16**, 106.

I.C.I., Plastics Division, for the sample of 36,000 molecular weight polymer, and to the Carnegie Trust for a research scholarship which has made it possible for one of us (N. G.) to carry out this work.

Summary.

The thermal degradation of polymethylmethacrylate has been investigated using a new type of dynamic molecular still. The purely thermal degradation reaction was isolated from oxidative fission and repolymerisation by keeping the pressure in the still as low as possible.

There is no fall in molecular weight, at least in the initial stages of the reaction, and very small amounts of 1 : 4-diamino anthraquinone stop the reaction almost completely. This shows that the mechanism is reverse polymerisation which is a chain reaction, involving radicals.

The rate of production of monomer is quite independent of the molecular weight of the polymer sample. Also the nature of the end groups alters the rate of the reaction to a marked extent. This undoubtedly shows that fission is initiated by breaking at the ends of the chains.

The degradation theories put forward up to the present, namely, degradation by the random breaking of chains or by "stepwise degradation" (preferred or exclusive breaking at the ends) are ruled out because there is no fall in molecular weight at the beginning of the reaction.

There is a very marked decrease in the rate of production of monomer as the reaction proceeds- this has been linked up qualitatively with the increase in the energy of activation during the course of the reaction and with the fall-away in molecular weight of the highest molecular weight samples.

All molecular weights were determined osmotically.

Résumé.

La dégradation thermique de méthacrylate de polyméthyle a été étudiée en employant un nouveau type de cornue dynamique moléculaire. De faibles quantités de 1-4-diamino-anthraquinone inhibent la réaction ; on en conclut que le mécanisme est l'inverse de la polymérisation, c'est à dire une réaction en chaîne, comportant des radicaux. La coupure est amorcée en bout de chaîne. La possibilité d'une dégradation par coupure au hasard dans les chaînes ou par recul de la réaction est élimine, du fait qu'il n'y a aucune chute du poids moléculaire au début de la réaction.

Zusammenfassung.

Der thermale Abbruch von Polymethylmethacrylat ist mit Hilfe einer neuen Art dynamischer molekularer Vakuumdestillation untersucht worden. Kleine Mengen an 1, 4 Diaminoanthrachinon verzögern die Reaktion, woraus gefolgert wird, dass die Reaktion als umgekehrte Polymerisation verläuft, d.h. als Kettenreaktion mit Radikalen. Die Spaltung wird am Ende der Kette eingeleitet. Ein Abbruch durch regelloses Brechen der Ketten oder stufenweiser Abbruch sind ausgeschlossen, da am Anfang der Reaktion keine Abnahme des Molekulargewichtes stattfindet.

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OXIDATIVE DEGRADATION OF POLYMERIC MATERIAL.

By Arthur V. Tobolsky.

Received 15th December, 1947.

The degradation of polymeric materials subject to heat and air is, at first sight, a rather unpleasant, intractable subject. During degradation or ageing of hydrocarbon rubbers, plastics and fibres, profound physical changes occur as well as important chemical changes. The isolation of exact chemical species during degradation is in most cases impossible, and even the determination of functional groups that form during degradation presents formidable problems. The evaluation of the physical changes has in the past been largely confined to standard engineering tests such as measurement of tensile strength and elongation at break after oven ageing or oxygen-bomb ageing.

During the past few years certain new facts have been discovered and new ideas have been developed which make it possible to treat this subject from a more-or-less unified point of view. We shall first discuss the new experimental facts, then outline the theory which seems to unify these facts, and finally discuss possible applications of these new chemical ideas.

New Chemical Facts.—From the purely chemical point of view, many recent ideas arising from the study of the oxidation of low molecular-weight hydrocarbons apply equally well to polymeric degradation.

1. The pioneering work of Farmer [1] established that, in the initial stages of oxidative degradation, practically all the chemically-combined oxygen is combined in the form of hydroperoxides.

2. Studies of the kinetics of oxygen absorption [2] indicate that the rate is first order in oxygen pressure at low oxygen pressures and zero order in oxygen pressures at high pressures. Furthermore the rate of oxygen up-take is catalysed by peroxides and hydroperoxides and inhibited by quinones. Bolland and Gee [2] explain these facts by a chain mechanism.

3. During the secondary stages of oxidative degradation the formation of the carbonyl group can be demonstrated.

4. It was demonstrated that the mechanisms of polymerisation and oxidative degradation are intimately related. Medvedev and Zeitlin [3] showed that during polymerisation of styrene in the presence of oxygen, the rate of formation of benzaldehyde and formaldehyde was proportional to the rate of formation of polymer. It was also shown that during the polymerisation of vinyl compounds such as diphenyl ethylene, styrene and methyl methacrylate in the presence of oxygen, oxygen acts as a temporary inhibitor, but that subsequently polyperoxides were formed in which the peroxide link is incorporated in the chain molecules.[4] Furthermore, it was shown that peroxides, light and oxygen can simultaneously catalyse polymerisation of monomer and degradation of polymer under identical conditions.[5]

[1] Farmer, *Trans. Faraday Soc.*, 1940, **38**, 341, 348, 356.
[2] Bolland and Gee, *ibid.*, 1946, **42**, 236.
[3] Medvedev and Zeitlin, *Acta Physiochim.*, 1945, **20**, 3.
[4] Bovey and Kolthoff, *ibid.*, 1947, **69**, 2143.
[5] Spence and Ferry, *J. Amer. Chem. Soc.*, 1937, **59**, 1648; Mesrobian and Tobolsky, *ibid.*, 1945, **67**, 785; Taylor and Tobolsky, *ibid.*, 1945, **67**, 2063.

5. The process involved in oxidative degradation must be described in terms of several concurrent reactions occurring at nearly equal rates over wide ranges of temperature.[5, 6]

Molecular Morphology Underlying Changes of Physical Properties during Oxidative Degradation.—The changes in physical properties of polymers during oxidative degradation is in large part due to the simultaneous occurrence of disaggregative reactions, such as scission and depolymerisation which tend to lower the molecular weight, and aggregative reactions such as cross-linkage, branching and further polymerisation which tend to raise molecular weight. Cyclisation tends to have somewhat similar physical effects as the aggregative reactions. If during ageing or degradation the disaggregative reactions are faster than the aggregative reactions, the polymer will tend to soften. If the reverse is true, the polymer will tend to harden and become infusible and insoluble.

Recent attempts to study these effects more precisely have employed the following physical methods.

1. The isolation of the disaggregative reactions can presumably be studied by following the molecular-weight changes during degradation in dilute solution where the polymer molecules are kept sufficiently far apart so that aggregative reactions are suppressed. The main difficulty with this method is in finding a completely inert solvent. The trick of keeping the molecules far apart and thus favouring disaggregative reactions can be put to use by employing swelling oils during reclaiming of synthetic rubbers which tend to harden during oxidative degradation in the unswollen state.

2. The net effect of the aggregative and disaggregative reactions can be studied by following the molecular-weight changes during oxidative degradation of thin polymeric films. If the products of degradation remain soluble, these changes can be followed by the usual viscosimetric-osmometric methods. If the products are insoluble, the changes in degree of cross-linkage can be followed by sol-gel measurements and swelling index of the gel.

3. For vulcanised rubbers, the scission reactions can be measured by relaxation of stress at constant elongation.[6] The net effect of scission and cross-linking can be measured by periodic measurement of the modulus at high temperatures. The manner in which these competing reactions combine to alter the structure and mechanical properties of synthetic rubbers at elevated temperatures is exemplified by the interpretation [7] of permanent set in rubbers maintained at constant length at elevated temperatures.

Mechanism and Kinetics of Autoxidative Processes.—The studies of the kinetics of oxygen absorption and the rate of formation of hydroperoxides has proved to be an extremely powerful tool in elucidating the mechanism of autoxidation. In Bolland's studies [8] of the autoxidation of ethyl linoleate, he concludes that a chain reaction is involved where the growth and termination steps are as follows: (RH signifies ethyl linoleate, the hydrogen in question being the α-methylenic hydrogen):

GROWTH

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \quad (2)$$
$$RO_2^\bullet + RH \rightarrow ROOH + R^\bullet \quad (3)$$

TERMINATION

$$R^\bullet + R^\bullet \rightarrow R{-}R \quad (4)$$
$$RO_2^\bullet + R^\bullet \rightarrow RO_2R \quad (5)$$
$$RO_2^\bullet + RO_2^\bullet \rightarrow RO_2R + O_2 \quad (6)$$

The initiation step at the very beginning of oxidation is taken to be

$$RH + O_2 \rightarrow R^\bullet + HO_2^\bullet.$$

[6] Tobolsky Prettyman and Dillon, *J. Appl. Physics.*, 1944, **15**, 380.
[7] Andrews, Tobolsky and Hanson, *ibid.*, 1946, **17**, 352.

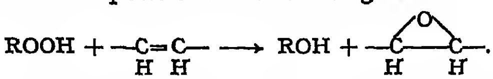
As autoxidation proceeds, the important initiation step is believed to be the bimolecular decomposition of the hydroperoxide

$$2ROOH \rightarrow R^{\bullet} + \text{other products.}$$

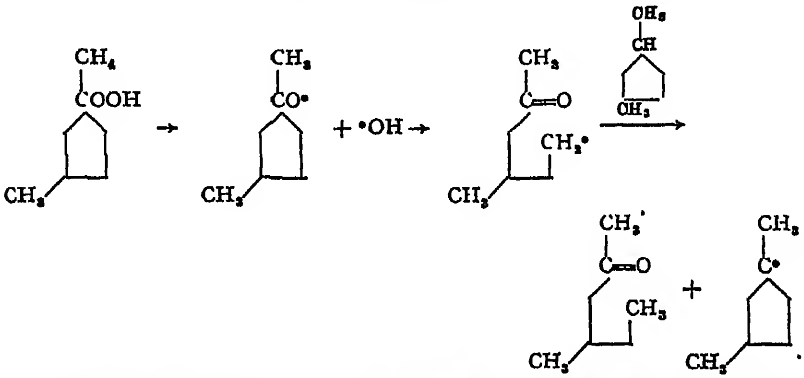
The benzoyl peroxide-catalysed oxidation is initiated by the unimolecular decomposition of the peroxide to give radicals.

These elementary reactions apparently explain satisfactorily the kinetics of oxygen absorption and hydroperoxide formation. The rate constants for hydroperoxide and benzoyl peroxide decomposition can be independently verified.

Subsidiary Reactions.—During the radical-chain autoxidations described in the last section, the active materials $R^{\bullet}$, $RO_2^{\bullet}$ and ROOH are formed. These can take part in important subsidiary reactions. In olefinic systems Farmer postulates the following reaction:



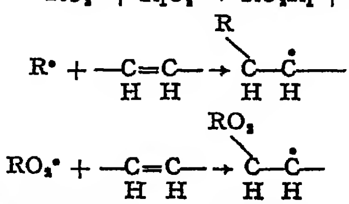
George and Walsh[8] postulate a very important mechanism for the decomposition of hydroperoxide by interpretation of the products formed during oxidation of 1 : 3-dimethyl cyclopentane.



The radicals $R^{\bullet}$ and $RO_2^{\bullet}$ can engage in all the well-known radical reactions—namely, addition to one another or to double bonds, mutual disproportionation or self-dismutation and abstraction of an atom (e.g. H or Cl) from saturated molecules. The relative importance of the radicals $R^{\bullet}$ and $RO_2^{\bullet}$ depends on the temperature and oxygen concentration.

Aggregative and Disaggregative Reactions.—The simultaneous aggregative and disaggregative reactions which are largely responsible for the changes of the mechanical properties of polymer subject to degradative conditions of heat, air and light can be understood in terms of the chemical mechanisms described above. The following aggregative reactions are of obvious importance:

$$R^{\bullet} + R_1^{\bullet} \rightarrow R—R_1$$
$$RO_2^{\bullet} — R_1^{\bullet} \rightarrow RO_2R_1$$
$$RO_2^{\bullet} + R_1O_2^{\bullet} \rightarrow RO_2R_1 + O_2$$



[8] George and Walsh, *Trans. Faraday Soc.*, 1946, **42**, 94.

Under controlled conditions these reactions are the basis of radical polymerisations, radical vulcanisations, cyclisation and the formation of polyperoxides. On the other hand these same reactions are the cause of the deleterious heat-hardening and ageing of synthetic rubbers such as Buna—S and Buna—N.

Various mechanisms have been proposed for the disagregative reactions, each of which may be preponderatively operative under certain conditions and which may compete under other conditions. For example, at sufficiently high temperatures, and preferably in the absence of oxygen, polymers such as polymethylmethacrylate, polystyrene and polyisoprene will depolymerise with large yield of monomer. The mechanism is believed to be similar to the mechanism widely accepted for the pyrolysis of hydrocarbons :

$$—CH_2CHXCH_2CHXCH_2\underset{X}{\dot{C}}—CH_2CHXCH_2CHX— \rightarrow$$
$$—CH_2CHXCH_2CHX^{\bullet} + CH_2{=}CX—CH_2CHXCH_2CHX—$$
$$—CH_2CHXCH_2CHX^{\bullet} \rightarrow —CH_2CHX^{\bullet} + CH_2{=}CHX, \text{ etc.}$$

Whether the radical which is responsible for the initial break is at the end of the chain or some place along the chain can only be decided by experiment.

If peroxy links exist along the polymeric chains these will be particularly susceptible to cleavage resulting in a lower molecular weight :

$$—CH_2CHXCH_2CHXCH_2CHXOOCH_2CHXCH_2CHX— \longrightarrow$$
$$CH_2CHXCH_2CHXCH_2CHXO^{\bullet} + {}^{\bullet}OCH_2CH_2CHXCH_2CHX— \longrightarrow$$
$$CH_2CHXCH_2CHXCH_2^{\bullet} + CHXO + CH_2O + {}^{\bullet}CH_2CHXCH_2CHX—$$

Medvedev and Zeitlin [8] propose the possibility of self-dismutation of the radical $RO_2^{\bullet}$

$$—CH_2CHXCH_2CHXCH_2CHXOO^{\bullet} \longrightarrow$$
$$—CH_2CHXCH_2CHX^{\bullet} + CH_2O + CHCO.$$

If this type of dismutation exists it could, of course, also occur in the middle of a chain.

At lower temperatures the most important mechanism is probably the decomposition of hydroperoxides as proposed by George and Walsh.[8]

Applications and Speculations.—From the point of view of maintaining unchanged the physical properties of polymeric materials such as rubbers, resins and fibres, the oxidative degradations described in this article are, of course, to be regarded as undesirable. The theory of inhibition of these reactions is at present being elucidated by Bolland [9] and collaborators.

Recent studies [10] on the effect of chemical structure of polymers on their relative susceptibility to oxidative degradation have revealed that the presumably inert structure of polyethylene is subject to surprisingly rapid autoxidation. Any modification of the straight paraffinic chain by introduction of carbon-to-carbon double bonds or methyl groups appears to accelerate the rate of oxidation (methyl groups particularly appear to accelerate the rate of scission, whereas double bonds accelerate both scission and cross-linking, particularly the latter). Most other side chains seem to decelerate the rate of oxidation.

From many other points of view the oxidative degradation of polymers is desirable and necessary. For example, the plasticisation of rubbers by milling or by heat-softening is an essential step in the processing of these materials. Further elucidation of these processes and the role of chemical plasticisers would be most illuminating. The vulcanisation of saturated polyester rubbers by benzoyl peroxide is a striking example of another useful role of these reactions.

[9] ten Have and Bolland, *Trans. Faraday Soc.* (in press).
[10] Mesrobian and Tobolsky, *J. Polymer Sci.*, 1947, **2**, 463.

The possibilities of equilibrium between polymerisation and depolymerisation [11] and equilibrium copolymerisation under certain conditions have also been suggested.

As the mechanisms described in this article become more fully elucidated it seems certain that these reactions, and particularly the degradation of polymeric materials, will be more fully utilised in the synthesis of important chemicals. For example, it has been suggested [12] that *trans*-polyisoprene may possibly be an *in vivo* and *in vitro* source of many terpenes and terpenoids. New monomers have been prepared by chlorination followed by depolymerisation of polymeric chains.[13]

Résumé.

On critique brièvement les mécanismes de radicaux qui prennent place lors de la dégradation de polymères.

Zusammenfassung.

Die Radikalmechanismen für den Abbau von hochpolymeren Substanzen werden kurz besprochen.

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[11] Tobolsky, *J. Chem. Physics*, 1944, **12**, 402.
[12] Tobolsky, Castro, Stein and Sacher, *J. Polymer Sci.*, 1947, **2**, 246.
[13] Bachman, *et al.*, *J. Org. Chem.*, 1947, **12**, 108.

OXIDATIVE DEGRADATION OF GR-S IN SOLUTIONS.

BY MISS J. LACAU AND MICHEL MAGAT.

Received 13th August, 1947.

Some time ago, Taylor and Tobolsky [1] published a very important paper on the radical chain processes in polymerisation and depolymerisation of vinyl and diene compounds. From the principle of microscopic reversibility they were led to the conclusion that "a splitting can first occur at any place along the chain, followed by an unravelling of the chain by a continued splitting-off of monomer units." This reaction can be induced by free radicals, which may be either extraneous to the polymer molecule or produced in the chain itself by oxygen. The fundamental role of oxygen is (in this theory) to produce and maintain a supply of free radicals. Oxygen acts chiefly as a catalyst, but is, at least partly, "chemically combined with the polymer by the radical recombination of hydrocarbon radicals with —OOH fragments."

This conception of the role of oxygen is widely different from the ideas of Farmer [2] according to whom the initial step is a peroxide formation followed by a decomposition of the peroxide, leading either to an internal cyclisation, or to a chain scission, or to a bridge formation between two polymer molecules.

In view of the practical and theoretical importance of the question, we undertook some experiments in order to decide between the two theories. In the course of our work it appeared that the problem was

[1] Taylor and Tobolsky, *J. Amer. Chem. Soc.*, 1945, **67**, 2063.
[2] Farmer, *Trans. Faraday Soc.*, 1946, **42**, 228.

much more complex than it appears in either theory. Hence this paper is not to be considered as a final statement on the subject, but rather as a progress account. Nevertheless it already gives a certain basis for theoretical conclusions on the possible mechanism of oxidative degradation of high polymers.

Experimental.

In order to eliminate the intermolecular bridge formation and thus simplify the problem, we investigated the thermal degradation of polymer in toluene solution. The polymer used was a commercial GR- S, which was carefully purified and fractionated in 7-8 fractions. Naturally the elimination of the inhibitor is most important. This is achieved by repeated acetone extraction and twofold precipitation. The degradation was followed viscosimetrically. The molecular weights were calculated, using the empirical relation between the viscosity and molecular weight as determined by Scott and Magat [3] and confirmed in this laboratory on the particular batch used. The peroxides were determined by the ferrous thiocyanate method,[4] using a Meunier-type colorimeter [5] giving readings reproducible to 1 in a 1000. If applied under identical conditions this method gives results reproducible to 2-3 % All the experiments were carried, out in electric ovens in the dark. The temperature was constant to $\pm$ 2° during the whole experiment.

Two sets of experiments were performed. In set A, 5-7 cc. of the solution were sealed in Ostwald-type viscosimeters of 23-25 cc. content as described by Zhukov, Komarov and Sibiriakova [6] and Tobolsky and Mesrobian.[7] Using these devices the heating could be interrupted at any time, the viscosity determined without the polymer coming in contact with fresh oxygen and the heating continued afterwards. At the end of the experiments the viscosimeters were opened. the final molecular weight checked if necessary on a standard Ostwald viscosimeter, and the peroxide determined as described. Although the viscosities measured in the sealed-type viscosimeters are not as precise as those measured in the usual way, this method offers the advantage that the points corresponding to a given degradation are obtained under absolutely identical conditions. However, this type of experiment does not allow the determination of the variation of peroxide content in the course of the reaction. For this reason, in the second set of experiments (B), 5-6 cc. of the solutions were sealed, under conditions as closely identical as possible, in test-tubes of 55 cc. content. The test-tubes were placed horizontally and close together in the oven. They were opened one at a time after various heating periods and the intrinsic viscosity and peroxide content determined. The advantage of this set of experiments is that the heating proceeds without interruption ; the disadvantage is that it is naturally impossible to seal the test-tubes, pertaining to one run, under absolutely identical conditions.

While being sealed, viscosimeters and test-tubes were put into liquid air. This precaution is necessary, because otherwise there is a risk of solvent vapour catching fire and using up a part of the oxygen. When sealed under vacuum, the solution was allowed to boil for a few seconds in order to eliminate the dissolved air, and then frozen out again. It is of course necessary, in calculating the amount of oxygen to correct for the temperature.

Results.

In order to test the reproducibility, 5 viscosimeters sealed in air, under identical conditions and containing the same solution were placed together in the oven. Fig. 1 gives the variation of the molecular weight with time, for those five viscosimeters. The plain line corresponds to type B experiments made under identical conditions. We see that the agreement between the different viscosimeters is satisfactory, but that the degradation in test-tubes goes somewhat faster. We think that this is due to the fact that a certain time is necessary for the viscosimeters and the oven to revert to the experimental temperature,

[3] Scott and Magat (in preparation). Scott, *Thesis* (Princeton, 1944).

[4] Bolland, Sundrilangam, Sutton and Tristram, *I. Rubber Inst. Trans.*, 1941, 17, 29.

[5] Jobin and Yvon, Paris. We thank Prof. Aubel for permission to use his apparatus.

[6] Zhukov, Komarov and Sibiriakova, *Kolloid Z.* (*U.R.S.S.*), 1935, 1, 9.

[7] Mesrobian and Tobolsky, *J. Amer. Chem. Soc.*, 1945, 67, 785.

after each interruption of the experiment rather than to the existence of an induction period. This interpretation is suggested by two observations: the rate of degradation in A type experiments is not significantly influenced by the number

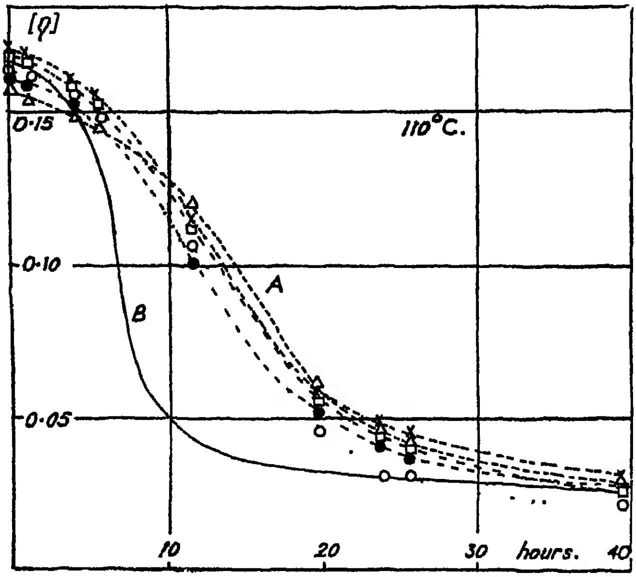

FIG. 1.—Reproducibility of degradation measurements. A: viscosimeters; B: test-tubes.

of interruptions; the difference between the two sets decreases with temperature while the induction period increases.

Tobolsky and Mesorbian found that, in absence of air, monomer molecules in radical form were able to induce a depolymerisation of polystyrene. If the

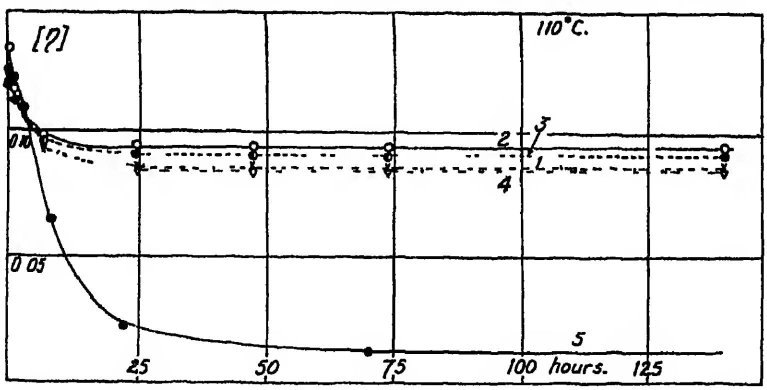

FIG. 2.—Effect of added free radicals on the rate of degradation *in vacuo*. x, 0·01 % of benzoylperoxide added; Δ, 1 % Diproxyd added.

conclusions of Taylor and Tobolsky are correct, the same effect ought to be observed on addition of any type of free radicals or radical-producing substances, e.g. benzoyl peroxide, or even modifiers like dodecyl mercaptan or di-*iso*propyl-xantogen disulfide (Diproxyd). We have tried to check this conclusion in a type A experiment. Five viscosimeters, containing 5-7 cc. of a 5 g./l. solutions of GR-S (M.W. 400,000) were used. No. 1-4 were sealed under high vacuum

(extinction of a Crooke's tube). No. 1 contained a pure solution, No. 2 and 3 contained in addition, 1 % of benzoyl peroxide (calculated on the weight of the polymer); No. 4 contained 1 % of Diproxyd in addition; No. 5 contained the solution sealed in air in order to provide a check. The results are shown in Fig. 2. One can see immediately that in *absence of air* neither benzoyl peroxide nor Diproxyd produce a degradation of the polymer. This was confirmed also in expts. with quantities of peroxide and Diproxyd 5 to 10 times greater. In another run, it was found that in *presence of air* the Diproxyd accelerated the decomposition, particularly in the beginning.

It was found in a subsequent experiment that the decomposition of benzoyl peroxide is a reaction of nearly first order (possibly somewhat lower) in agreement with Cass.[8] The half-life time is about 30 hr. at 80° c.; it is much shorter than the half-life time of degradation at this temperature (85 hr.). Hence it may be possible that the decomposition of benzoyl peroxide proceeds too quickly to induce the depolymerisation.

TABLE I.—FINAL MOLECULAR WEIGHTS AFTER DEGRADATION IN AIR AT ATMOSPHERIC PRESSURE.

Initial M.W.	900,000			400,000	100,000
Conc. g./l.	1·15	5	10	5	5
Temperature ° c.	Final Molecular Weight.				
130°	—	8,000	—	7,000	2,000
110°	11,000	5,000	11,000	5,000	11,000
90°	—	11,000	—	6,000	6,000
72°	—	—	—	7,200	—

It is hence obvious from this experiment that the peroxides formed along the polymer chain itself play a special role. The question now arises whether they simply play the role of a particularly active catalyst or are chemically responsible for the scission. In our opinion two experiments can shed light on this question. Let us assume that the peroxides play simply the role of chain initiators for polymer scission. Then, when the reaction has once started, the depolymerisation would proceed till the equilibrium molecular weight corresponding to $\partial F/\partial n = 0$ is reached, n being the number of monomers in the chain.[9]

This equilibrium molecular weight depends on the temperature and is smaller the higher the temperature. It ought to be independent of the initial molecular weight and only slightly dependent, if at all, on the concentration. We have determined for a series of temperatures and fractions the final molecular weights after *degradation in presence of air*. The results are summarised in Table I. One can see, that the final molecular weights do not depend neither on the concentration nor on the initial molecular weight; nor do they depend on the temperature.

On the other hand if we assume that the peroxides act only as catalysts, the final molecular weight ought to be independent of the amount of

[8] Cass, *J. Amer. Chem. Soc.*, 1946, 68, 1977.

[9] That such an equilibrium molecular weight does exist is obvious from thermodynamical reasons, if one considers the two limiting cases: (*a*) the solution contains n uncombined monomers; then the entropy (in addition to vibrational terms) is the entropy of the n monomers while the internal energy (binding energy of monomers) is zero. Hence $\Delta F = -T\Delta S_m$; (*b*) the monomers are connected to form a single-polymer molecule. The entropy is that of a single polymer of a chain length n, $\Delta S_n < \Delta S_m$, but the internal energy is $(n - 1)$ times the bond energy h, $\Delta F = (n - 1) h - T\Delta S_n$. Hence, for each binding energy and each temperature there exists a chain length corresponding to the lowest ΔF value.

oxygen present, provided there is enough of it to combine, at least once, with each chain. This conclusion also is in disagreement with the experiment as can be seen from Fig. 3, where we have plotted the final molecular weights for a temperature of 110° C. as a function of the initial amount of oxygen. A certain independence of the amount of oxygen exists only for relatively high pressures (above 100 mm. Hg).

From the foregoing we arrive at the conclusion that the Taylor-Tobolsky concept does not apply to the GR—S degradation in the temperature region of 70-140° C. It may, however, apply at higher temperatures. Our results tend to confirm the ideas of Farmer, that the scission is chemically related to the decomposition of peroxides. If the degradation appears to be a chain reaction, it is only because the peroxide formation (and possibly the decomposition) is autocatalytic.[10]

This close relationship between the degradation and the peroxide formation can also be seen from Fig. 4 which shows, for a type B experiment, the connection between the molecular weight variation and the amount of peroxide formed as a function of time. In the experiment carried out at 80° C. an abnormally long induction period for degradation was observed. An equally long induction period was found for the peroxide formation.

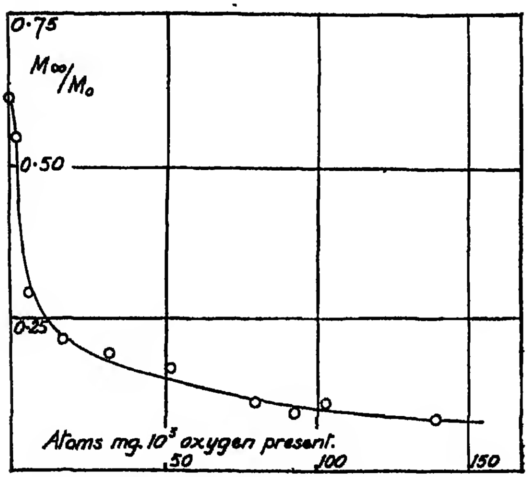

FIG. 3.—Final molecular weight/initial molecular weight as function of amount of oxygen present.

This figure demonstrates a further point. It might be expected, *a priori*, that the amount of peroxides present in the solution would, after being very small in the beginning, increase with time and drop to zero again when all the oxygen is used up. At low oxygen pressures in test-tubes and at any pressure in the viscosimeter, the amount of peroxide at the end of the degradation did in fact drop to zero. But in test-tubes, sealed at atmospheric pressure, the peroxide amount increased as long as there was a noticeable decrease of the molecular weight. Eventually a point was reached where the molecular weight *and* the amount of peroxide both became constant.

The remaining peroxides were very stable. They did not measurably decompose when kept in the dark for a week at room temperature. This rather unexpected result was confirmed in 4 independent runs. We do not yet know the cause of this discrepancy.

Only a small fraction, if any, of detectable peroxides can be used for degradation. The following experiment was performed to demonstrate this point. A test-tube containing 20 cc. of solution and sealed under atmospheric pressure was heated to 140° C. for 1 hr. The molecular weight dropped from 400,000 to 30,000 and the solution was found to contain over $1{\cdot}5 \times 10^{-4}$ g. of peroxide. The solution was then resealed under 5 mm. air pressure and heated again to 140° C. for several hours. On reopening no peroxide was detected, but the molecular weight dropped only from 30,000 to 26,000, i.e. to 86 % of its previous value. If a virgin

[10] Bolland and Gee, *Trans. Faraday Soc.*, 1946, 42, 236.

polymer were used at 5 mm. air pressure one would expect, according to Fig. 3 a molecular-weight drop to 27 % of its initial value. Hence the oxygen present can more than account for the degradation observed.

TABLE II.—PERCENTAGE OF AVAILABLE OXYGEN USED FOR SCISSION.

Air pressure (mm. Hg)	4	12	26	56
% oxygen used on scission	10-30	6-20	3-10	2-7

That a partially-degraded polymer is less susceptible to further degradation than a virgin one, is not an isolated observation. Farmer and Sundralingam[11] have already pointed out that the number of oxygen atoms absorbed per bond broken increases with the oxygen intake. We have found in our experiments on degradation under various pressures, that the percentage of available oxygen used for scission decreases when the pressure increases (see Table II). Hence one arrives at the following conclusions: oxygen first attacks the polymer molecule in those places that are most susceptible to scission, forming a very short-lived peroxide. Later on, other points are peroxidised too. The decomposition of these peroxides is slower. During rearrangements, points susceptible to scission may be destroyed. Under certain conditions a part of these can be converted to a form relatively stable at room temperature. In preliminary experiments the heat of activation for the formation of this second type of peroxides as deduced from the initial rates seems to be about 20-25 kcal., while Bolland and Gee found 26 kcal. for the oxidation of ethyl linoleate.

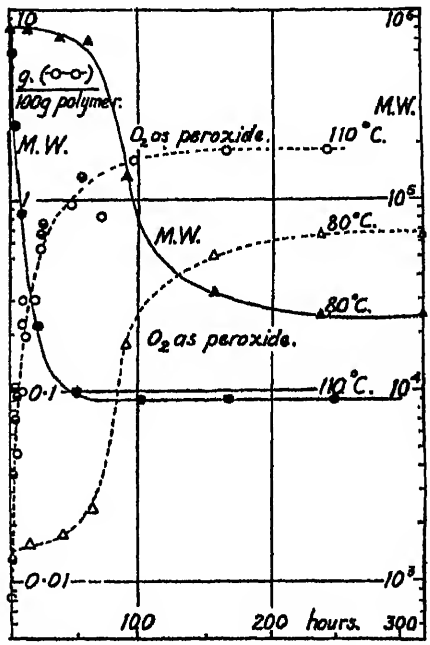

FIG. 4.—Variation of the peroxide content and of the molecular weight as function of the time at 80 and 110° C.

From a formal point of view the situation is analogous to the one observed in the adsorption of gases on crystals, where first the active points, and only later the less active ones, are covered by the adsorbed layer.

These conclusions are in agreement with those of Farmer (loc. cit.). A fairly rare and direct reaction, possibly an attack on double bonds, leads to the formation of unstable peroxides, while the bulk of the oxygen attacks the carbon atoms in the α-position and leads to stabilised peroxides.

Let us now consider what conclusions about the mechanism can be drawn from the kinetics of degradation and the kinetics of formation of the unstable peroxides.[12] The former was investigated fairly thoroughly at atmospheric pressure, but only preliminary data are available concerning the oxygen-pressure dependence. The following points can be considered as established.

[11] Farmer and Sundrilangam, *J. Chem. Soc.*, 1943, 126.
[12] Lacau, *Compt. rend.*, 1947, 224, 917.

(1) The only formula found so far that describes the reaction rate by a relatively constant value of K, is the formula for chain reactions:

$$K = \frac{1}{\theta} \log \frac{M_0 - M_t}{M_t - M_\infty}, \quad \theta = t - t_m$$

where M_0 is the initial molecular weight, M_∞ the final molecular weight, M_t the molecular weight at the time t and t_m the time corresponding to the maximum rate dM/dt.

Some typical degradation curves at different temperatures are reproduced in Fig. 5.

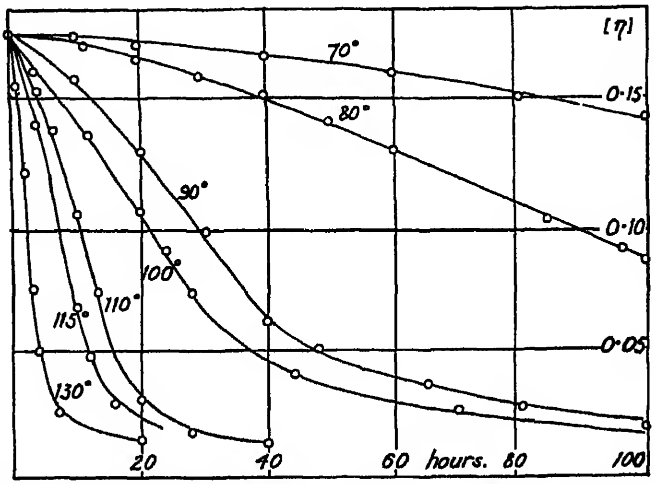

FIG. 5.—Variation of the viscosity as function of heating time for different temperatures.

(2) The log of the maximum rate of viscosity variation $(d\eta/dt)_m$, plotted against $1/T$, gives a straight line for temperatures lying between 70 and 140° C., as shown in Fig. 6. From the slope, an overall activation energy of 18·9 kcal. can be deduced. This figure is lower than that given by Bolland and Gee for the overall activation energy of the catalysed peroxidation of squalene. We think that one is entitled to conclude that the activation energy of decomposition of peroxide is very low, and even that the free energy of formation of unstable peroxides is most probably lower than that of more stable ones.

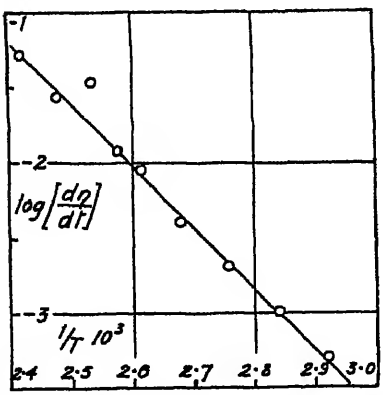

FIG. 6.—Maximum degradation rate as function of temperature.

(3) The rate of degradation expressed as the number of scissions per unit of time is independent of the chain length, at least between M.W. 50,000 and 1,000,000. The molecular weight drops to half its initial value in the same time-interval, whatever the initial weight. This is an additional argument against the Taylor-Tobolsky theory. Indeed, if a single free radical could cause

the unravelling of the chain, the degradation ought to go faster if the same number of monomers are combined in a few long chains, than if they are combined in a larger number of shorter chains. On the contrary it is consistent with the idea that certain points, particular double-bond configurations for instance, are more easily attacked by oxygen than others, if the number of such places is independent of the chain length. Hence, it could hardly be the double bonds in the vicinity of branches, since it seems reasonable to assume that the proportion of branches increases with the molecular weight.

(4) The rate of degradation is of zero order with respect to the polymer concentration, for concentrations lying between 1 g./l. and 10 g./l. This is in agreement with the active centre picture outlined above.

(5) In experiments made under 760 mm. air pressure, a certain induction period was observed that never appeared in runs made at 80 mm. or below. This would indicate, if confirmed by further experiments, that oxygen may act as an inhibitor, as it is usually observed in chain reactions going over to a free-radical mechanism.

(6) The maximum rate of degradation decreases somewhat with oxygen pressure, but the relation is definitely not linear. This is consistent with the inhibition action of oxygen through the reaction of oxygen with the chain-carrying free radicals.

We think that the following two points can be considered as established.

(*a*) The formation of "unstable" peroxides is an autocatalytic process: it was established that the succession of reactions — formation of peroxides, their decomposition, scission — form an overall autocatalytic process. If the decomposition were an autocatalytic process and the formation were not, the supply of peroxides would proceed at a slower rate than the decomposition, and the formation would undoubtedly be the rate-determining step. Since we assumed that the formation was not autocatalytic, the overall reaction would not be an autocatalytic process.

(*b*) The more stable peroxides, or their decomposition products, may act as catalysts for the formation of unstable peroxides: we have found that the peroxides surviving the interruption of heating are not able to produce scission and hence belong to the family of "stable" peroxides. If they were not able to catalyse the formation of unstable peroxides, each interruption of heating would be followed by a new induction period for the degradation. This was never observed.

Summary.

It was ascertained that an addition of free radicals does not induce a degradation of polymers in solution in the temperature region of 70-140° C. This degradation is connected with the formation of very short lived peroxides, that are not identical in structure with the more stable peroxides which can be determined by the ferrous thiocyanate method.

The unstable peroxides are formed preferentially when only small amounts of oxygen are available. The formation reaction is autocatalytic. It can be catalysed by the "stable" peroxides or their decomposition products.

Résumé.

L'addition de radicaux libres ne provoque pas une dégradation de polymères en solution entre 70 et 140° C. La dégradation est liée à la formation de peroxydes à vies courtes, dont la structure n'est pas identique à celle des peroxydes plus stables, qui peuvent être determinés par la méthode au sulfocyanate ferreux. Les peroxydes instables sont formés de préférence lorsque de faibles quantités seulement d'oxygène sont disponibles. La formation est auto-catalytique; elle peut être catalysée par les peroxydes "stables" ou leur produits de décomposition.

Zusammenfassung.

Die Hinzufügung von freien Radikalen zu Polymerlösungen bei 70-140° C. leitet nicht den Abbau der Polymeren ein. Abbau ist mit der Bildung kurzlebiger Peroxyde verbunden, deren Struktur nicht mit der Struktur der stabileren Peroxyde, die mit Ferrothiocyanat bestimmt werden können, identisch ist. Die nicht-stabilen Peroxyde werden vorzugsweise gebildet, wenn nur geringe Sauerstoffmengen vorhanden sind. Ihre Bildung ist autokatalytisch und kann durch " stabile " Peroxyde und deren Zersetzungsprodukte katalysiert werden.

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Faculté des Sciences, Paris.

GENERAL DISCUSSION.

Mr. R. W. Hall (*Epsom*) (*communicated*) : The mechanism of polymer degradation put forward by Grassie and Melville appears to be of rather a specific character. Experiments on the degradation of polystyrene at 340° c. have led to different conclusions as to the nature of the degradation process. Our experiments were carried out both in sealed systems originally at 10^{-3} mm. pressure and in continuously-evacuated systems under a pressure of 10^{-3} mm. or lower throughout. The polymers used were laboratory samples made by thermally polymerising pure monomeric styrene in vacuum and were unfractionated.

Our main observations were :

(*a*) there was an initial rapid fall in the polymer intrinsic viscosity after which it decreased slowly and almost linearly with respect to time ;

(*b*) the rate of monomer production followed an experimental zero-order reaction over a wide range of the decomposition ;

(*c*) the time elapsing prior to the commencement of the zero-order monomer production was related to the chain length of the original polymers, high molecular-weight polymers requiring a greater time than low molecular-weight polymers ;

(*d*) the rate of monomer production appeared to be mainly independent of the original polymer chain-length, though there are indications of a minor relationship, e.g. the degradation constant for a polymer of intrinsic viscosity 5·8 was $5{\cdot}8 \times 10^{-5}$ mole/sec. while that for a polymer of intrinsic viscosity 64·9 was $5{\cdot}2 \times 10^{-5}$ mole/sec. ;

(*e*) very low molecular-weight polymers, i.e. polymers of intrinsic viscosity lower than about 2·0 showed an entirely different kinetic behaviour. The reaction was first order up to about 30 % decomposition after which, as in the methyl methacrylate degradation, the formation of monomer decreased sharply. It was also much more rapid than for higher polymers, e.g. a polymer of intrinsic viscosity 1·2 showed an initial rate constant of $16{\cdot}2 \times 10^{-5}$ mole/sec.

From these observations we conclude that the first step in the degradation of polystyrene is a rapid chain scission to shorter fragments which can then degrade step-wise to produce monomer. It is significant that the zero-order reaction commences when, as a plot of the intrinsic viscosity against time shows, the chain scission is substantially complete and comparatively stable (i.e. stable to further scission into lower molecular-weight fragments, but *not* stable to end-group fission) chain fragments remain. If such a " scission-stable " chain length at 340° c. is postulated then the observation that the rate of monomer production is almost constant over a wide range of molecular weights can be explained by the fact that there would be a similar number of chain fragments present per unit weight, irrespective of the original polymer chain length. At 340° c. the intrinsic viscosity corresponding to this " scission-stable " chain length

is between 3·0 and 4·0. From this we can immediately see that low polymers of intrinsic viscosity below this range will contain more chain-ends per unit weight than those above and so degrade to monomer much faster. This can be seen from the data in observations (*d*) and (*e*).

The experimental conditions under which our experiments were conducted would appear to rule out the possibility of oxidative degradation of the polymer. It was calculated that in our experiments the ratio of oxygen to polymer molecules was less than 1 : 10,000 and this would seem to preclude even a free-radical mechanism involving oxygen being the major factor operative. This is supported by the fact that the rate of monomer production in the degradation of vacuum-polymerised polymer in a vacuum of 10^{-3} mm. and under an air pressure of 1·0 mm., of air-polymerised and catalysed polymers under 10^{-3} mm., was practically the same in all cases.

Summarising, the contrasting features of this type of degradation when compared with that of polymethyl methacrylate are :

(i) degradation to monomer is preceded by a comparatively rapid breakdown to shorter chains which then proceed to split off monomer from their ends ;

(ii) the degradation follows a zero-order course for a substantial part of the decomposition, the rate varying only slightly with the original chain length ;

(iii) the rate of degradation is not so dependent upon the original polymer end-groups as in the case of methyl methacrylate, for chain scission creates new unsubstituted chain-ends which can split off monomer.

Dr. H. H. G. Jellinek (*London*) (*communicated*) : It is of interest to compare the experimental results obtained by Grassie and Melville with results on the thermal degradation of polystyrene in the bulk-phase which I obtained in the years 1942-1945 in the Department of Colloid Science, Cambridge. There are striking differences in the behaviour of polystyrene and polymethyl methacrylate during degradation in high vacuum. The first part of my work consisted in following the degradation of fractionated samples by viscosity and size-distribution measurements. These experiments were carried out over a range of temperatures from 250° to 340° C. The results cannot be reconciled with the random theory of breaking links. The degradation stops at a certain chain-length, which is different for different temperatures and initial chain-lengths ; the energy of activation is very low, the rate constants, which are independent of chain-length can be represented by the following Arrhenius eqn., $K' = 1{\cdot}3 \times 10^5 \times e^{-\frac{24,600}{RT}}$ sec.$^{-1}$; the distributions are narrower and the amount of monomer produced is 10^3 to 10^4 times higher than expected from the random theory. These results can be explained quite satisfactorily by assuming that each polymer chain has a number of weak points, which consist most likely of oxygen groups, the degradation sets in at these points leading to chain scission thereby producing active chain-ends which split off monomer units in rapid succession and eventually lose their activity. This reaction corresponds to the scheme used in polymerisation reactions, namely : (1) *initiation* : chain scission producing active chain-ends ; (2) *propagation* : production of monomer ; and (3) *termination* : loss of activity of the chain-ends. The number of monomer units produced per active chain-end could actually be ascertained and is higher at lower temperatures ; i.e. the termination reaction is favoured at higher temperatures. Another part of the work was concerned with measuring the amount of monomer produced, or the loss of weight a polymer sample suffers during degradation. These experiments were carried out in a specially-designed quartz-spring balance apparatus. They were conducted over a temperature range from 348 to 398° C. At these temperatures a different reaction takes place from that described above which may be termed "true" depolymerisation corresponding to the

reaction studied by Grassie and Melville; nevertheless, striking differences exist between the behaviour of polymethyl methacrylate and polystyrene. The chain scission at the weak points is completed very rapidly and then the true depolymerisation sets in. In contrast to polymethyl methacrylate the chains once activated do not depolymerise completely but either monomer is split off the chain-ends one after another in a stepwise manner or a limited number of monomer is split off. This is proved by the fact that the monomer production is of zero order up to 60-80 % monomer production, that is to say, the number of chain-ends remains constant over a very large part of the degradation. Also viscosity measurements confirm this conclusion. Further the rate constants for the same weight of fractions of different chain-length are inversely proportional to the chain-length i.e. proportional to the number of chain-ends present in the system, whereas the rate constants do not vary with chain-length in the case of polymethyl methacrylate. The polymethyl methacrylate should be a first- or higher-order reaction in respect to the disappearance of chain-ends since chain-ends disappear continuously; for a first-order reaction one has log $g_0/g = Kt$, where g_0 is the number of chain-ends at the start of the degradation and $g = g_0 - \frac{2n_{\text{monomer}}}{P_0}$ the number of chain-ends at the time t. A further difference in the behaviour of these two substances consists in the fact that the energy of activation remains constant over a range of chain-lengths from 500 to 2000 in the case of polystyrene, the rate constants can be expressed by the following Arrhenius equations:

Fraction.	$\lim\limits_{c \to 0} \eta/c$	Rate Constant.
F_V	4·1	$k_V = 10^{12.30} \times e^{-\frac{44,700}{RT}}$ mole./sec./basic mole.
F_{III}	9·0	$k_{III} = 10^{12.19} \times e^{-\frac{44,700}{RT}}$,, ,, ,,
F_{II}	16·0	$k_{II} = 10^{12.05} \times e^{-\frac{44,700}{RT}}$,, ,, ,,

The reaction, which was termed above true depolymerisation, can probably be described satisfactorily for different polymers like polystyrene and polymethyl methacrylate by one reaction scheme as follows:

(1) *Initiation:* or activation of a long chain molecule;
(2) *Propagation:* splitting off of monomer units;
(3) *Termination:* loss of the activity at the chain-end.

In the case of polymethyl methacrylate the termination reaction is negligible, whereas in the case of polystyrene the rate of propagation and termination are of the same order. This view is consistent with the activation energies observed, the energy for polystyrene being considerably higher than for polymethyl methacrylate.

In the case of polymers which behave like polystyrene during degradation the measurement of the rate constants gives a means for determining number-average M.W. of polymers, since the rate constant is proportional to the number of chain-ends present in a definite amount of polymer and the number of chain-ends in turn is inversely proportional to the chain-length.

Polyethylene which was also investigated in the quartz-balance apparatus over a range of temperatures from 375 to 436° showed also a zero-order reaction but the energy of activation varied with the M.W.,

increasing with increasing M.W., the rate constants can be represented by the following Arrhenius equations :

Grade.	Av. M.W.	Rate Constant.
2	23,000	$k_2 \quad 10^{18 \cdot 8} e^{-\frac{66,100}{RT}}$ g./100 g./sec
20	16,000	$k_{20} \quad 10^{11 \cdot 8} e^{-\frac{52,000}{RT}}$,, ,,
200	11,000	$k_{200} = 10^{12 \cdot 61} e^{-\frac{46,000}{RT}}$,, ,,

Also poly-α-methylstyrene was investigated in the same apparatus (M.W. 70,000) over a range of temperatures from 280 to 363° C. The curves for monomer production show characteristic differences from those of polystyrene. They show a zero-order reaction up to 30 % monomer production, the reaction then slows down and is accelerated in its later stages. The rate constants for the initial part of the reaction can be represented by the following Arrhenius equation

$$k = 1 \cdot 58 \times 10^{15} e^{-\frac{45,100}{RT}} \text{ g./100 g./sec.}$$

Cross-linked polystyrene (*m*-divinylbenzene) shows very long induction periods before degrading but eventually monomer is produced following a zero-order reaction. The length of the induction periods is a function of the amount of the cross-linking agent. Cross-linked polystyrene which was polymerised in the presence of benzoyl peroxide showed a considerably shortened induction period.

In conclusion it may be remarked that in the paper by Votinov, Kobeko and Marei referred to by Melville and Grassie the experimental results were evaluated according to the random theory of breaking links which, of course, is quite inadmissible.

Dr. F. C. Frank (*Bristol*) (*communicated*) : (1) In thermodynamic equilibrium at a given temperature, every polymer should have a definite vapour pressure of monomer (*inter alia*). For sufficiently high polymers this pressure should be independent of chain length and of the nature of the terminal groups. Any catalyst which influences the rate of attainment of equilibrium from the one side should influence it equally from the other. A free-radical terminal group on the polymer chain is such a catalyst. It is a catalyst for the equilibrium between polymer and monomer, and not a catalyst for the equilibria between polymer and lower polymers. Hence the effect observed by Grassie and Melville is inevitable and ought to have been foreseen by the earlier workers (though, of these, apparently only Taylor and Tobolsky [1] would have foreseen it). Degradation must occur in the manner observed as soon as (*a*) the pressure is pumped below the equilibrium vapour pressure, and (*b*) some of the polymer molecules acquire free-radical terminal groups of the same type as occur in the polymerisation process.

(2) The above statement about the effect of a catalyst is strictly true, but substances which induce polymerisation are often not strictly catalysts, being consumed in the reaction. Free radicals provide ideal catalysts if the growth of polymer molecules always ceases by chain transfer and not by termination reactions. (The ideal catalyst present in this case is not a substance, but the radicalism of the end of a polymer molecule.) If transfer of radicalism occurs, added free radicals can promote degradation by producing free-radical end-groups on previously "dead" polymer

[1] Taylor and Tobolsky, *J. Amer. Chem. Soc.*, 1945, 67, 2063.

molecules. If there is no transfer, radicals which "catalyse" polymerisation can fail to catalyse degradation.

(3) The vapour pressure of methyl methacrylate in equilibrium with the polymer is shown by Grassie and Melville's experiments to exceed 10^{-6} mm. Hg at 160° c. Theoretically we may anticipate the order of magnitude $10^8 \,.\, e^{-Q/RT}$ mm. Hg, where Q is the heat of polymerisation from gas phase. (Say, for methyl methacrylate, $\log p_{\text{mm.Hg}} \approx 8 - 4000/T$). The estimate could be much refined by deeper theoretical consideration. A precise measurement of this vapour pressure curve should be possible by a development of Grassie and Melville's technique, and would be a valuable contribution to the thermodynamics of polymerisation.

(4) Similar considerations apply to an equilibrium concentration of monomer with polymer in solution.

(5) Terminal bonds may be either easier or less easy to break than bonds in the middle of the chain. Only in the former case should thermal initiation occur at the ends, and the rate of degradation be sensitive to the nature of the terminal groups. In the latter case (and even in the former, for polymers of very high molecular weight), initiation should occur by scission anywhere in the chain. The rate of generation of monomer would then be proportional to molecular weight.

(6) When side groups are regularly disposed, the chain should degrade with different velocities in different directions. Polymers with only one natural direction of growth, say, R(—CHX—CH_2)—, will only degrade in one (the reverse) direction from a scission. This will be either direction according as the breakage chances to occur right or left of CHX. Likewise when the polymer has various possible modes of growth (radical- or ionic-growth mechanisms), it will be able to degrade in the same ways, with propagation velocities in the same ratio as the growth propagation velocities.

(7) Polymerisation is due to an excess of the rate of growth over the rate of degradation, and precise kinetic equations must take account of this. (Blatz and Tobolsky [2] do so for the particular case that no initiation step is required.) The true propagation constant for growth will exceed the apparent propagation constant by the factor $M/(M - M_{eq})$ where M expresses the actual monomer concentration and M_{eq} its equilibrium value. This becomes a serious correction at high temperatures, low concentrations, and when the free energy of polymerisation (in the given medium) is low. M_{eq} is also the ratio of the propagation rate constants for degradation and growth. Taylor and Tobolsky [1] have already remarked that the difference in activation energy for these two processes is the heat of polymerisation.

Dr. M. J. S. Dewar (*Maidenhead*) (*partly communicated*): It seems possible to draw further conclusions from the published experiments. Since the photopolymer degraded readily, the labile terminal group must be one present in photopolymer; and this can only be the unsaturated group (I) formed by disproportionation of radicals. Disproportionation will lead to unsaturation in half the terminated ends of polymers, the other half being saturated. But since photopolymer is formed by the growth of double radicals, each polymer molecule should contain, on average, twice as many unsaturated ends as catalytic polymer (formed by growth of single radical centres). Therefore the photopolymer should degrade twice as rapidly as the catalytic polymer, in agreement with Grassie and Melville's results:

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                        COOMe
                        |
MeOOC . CMe=CH—CMe-
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(I)

[2] Blatz and Tobolsky, *J. Physic. Chem.*, 1945, 49, 77.

Presumably fission at the dotted line in (1) occurs, giving two mesomeric radicals. In the catalytic polymer, similar fission should occur in chains terminated by phenyl, but present evidence suggests that the majority of chains will be initiated by PhCOO• radicals; the termination PhCOO . CH_2 . CMe(COOMe)〰〰 cannot split into *two* mesomeric radicals.

In the later phases of the polymerisation the majority of the remaining polymer molecules will not have sensitive ends; central fission of the polymer chains should then become important. This reaction, giving one mesomeric and one non-mesomeric radical, will be slower and have a higher activation energy; hence the "abnormal" decrease in rate of degradation. From Grassie and Melville's results (Fig. 4) we may deduce that the activation energy for this central chain-fission is about 42 kcal. Taking Evans and Tyrall's [3] figure of *ca.* 8 kcal. for the steric strain energy in polymethyl methacrylate, we may deduce that the resonance energy of the radical 〰〰 CH_2 . $\dot{C}$Me . COOMe is $\sim$ 30 kcal.,[4] and of the radical · CH=CMe . COOMe $\sim$ 10 kcal.

Moreover when chain fission occurs, the radicals formed will generally react with each other by a kind of primary recombination; but in this case they should disproportionate rather than recombine. Hence the net effect of chain fission will usually be to split the polymer molecule into two "normal" molecules (not radicals). The fall in molecular weight observed by Grassie and Melville in the later stages of the degradation would then follow. The fission produces a polymer fragment with an unsaturated end (I) which will degrade relatively rapidly.

It may be added that polymethyl methacrylate is probably unusual in its case of degradation, both because it is sterically strained and because it cannot easily undergo chain transfer. In most thermal degradations, chain transfer of the intermediate radicals with the polymer leads to extensive condensation and dehydrogenation.

Dr. C. H. Bamford (*Maidenhead*) (*communicated*): There is some evidence which suggests that the size of a free radical is one factor which determines whether combination or disproportionation will take place on reaction. The larger radicals appear to favour disproportionation. Thus when ketones in liquid paraffin solution at temperatures of 60° or higher are irradiated by light of wavelength 2500-3000 A., the large hydrocarbon radicals produced disproportionate quantitatively.[5] On the other hand with *iso*-octane as solvent most of the radicals combine. This argument, while admittedly not quite conclusive, because the structures of the hydrocarbon radicals are not known with certainty, suggests that Prof. Price's analogy[6] may be misleading. (Cp. Norrish's remarks in the General Discussion on Hydrocarbon Chemistry.[7])

If disproportionation occurs in the methyl methacrylate polymerisation, the rate of increase of viscosity at high light intensities becomes proportional to $I^{(1-\alpha)/2}$ (see eqn. (4), Bamford and Dewar [8]). Experimentally this relation is followed with $(1 - \alpha)/2 = 0{\cdot}10$, or $\alpha = 0{\cdot}80$. This agrees satisfactorily with the results of Baxendale, Bywater and Evans for fractionated polymethyl methacrylate, for which they find $\alpha = 0{\cdot}76$ (in benzene) and $\alpha = 0{\cdot}82$ (in chloroform). If, however, the termination reaction is combination, the rate should be proportional to $I^{\frac{1}{2}}$. Our results are therefore not compatible with the latter reaction.

[3] *J. Polymer Sci.*, 1947, **2**, 387.

[4] This agrees well with the high value found by Dr. Szwarc (this Discussion p. 39) for the resonance energy of benzyl, since copolymerisation experiments suggest that both radicals are of comparable stability.

[5] Bamford and Norrish, *J. Chem. Soc.*, 1938, 1531.

[6] This Discussion, p. 402.

[7] *Trans. Faraday Soc.*, 1939, **35**, 897.

[8] This Discussion, p. 310.

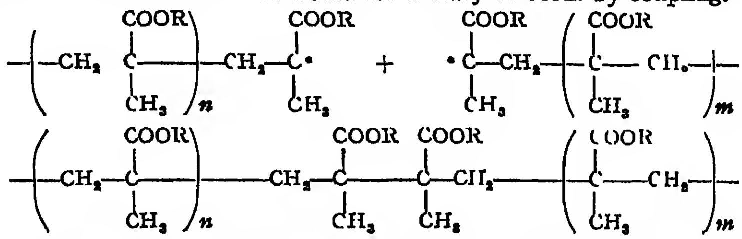
Prof. C. C. Price (*Notre Dame*) said: It seems quite definite that Grassie and Melville have demonstrated the presence of a thermolabile grouping in polymethyl methacrylate, which they have presumed to be at the end of a chain. There is, however, another alternative to be considered, depending on the nature of the bimolecular termination of growing chains. As pointed out by Prof. Norrish, his work satisfactorily demonstrates that two reactive paraffinic free radicals react almost exclusively by disproportionation.

$$2C_nH_{2n-1}^{\bullet} \longrightarrow C_nH_{2n-2} + C_nH_{2n}.$$

The free-radical succinic acid synthesis developed by Prof. Kharasch equally satisfactorily demonstrates that two free radicals with the odd electron, α to the carbethoxyl group, react almost exclusively by coupling.

$$2(CH_3)_2\dot{C}\,COOR \longrightarrow \begin{array}{l}(CH_3)_2\,C\,COOR\\ \quad\;\;|\\ (CH_3)_2\,C\,COOR\end{array}$$

It so happens that the active radicals in polymerising polymethyl methacrylate would be very similar in structure to the latter type so that reaction of two active chains would seem likely to occur by coupling.



For those polymer molecules deactivated in this way rather than by chain transfer or reaction with a catalyst fragment, there would thus be one link which, on thermal scission at high temperature, would produce *two* relatively stable radicals and would thus be energetically favourable. These two radicals could then, at high temperature, undergo reversal of the propagation step to liberate monomer.

Dr. G. Salomon (*Delft*) said: The assumption of equilibria in degradation reactions, involving dienes at high temperatures needs certain restrictions. Dienes, once formed at 150°-200° C., will dimerise very fast at these temperatures and as this reaction is purely thermal in nature and not catalysed by peroxides, the intermediate formation of a diene would exclude the establishment of any equilibrium with the polymer.

Dr. H. H. G. Jellinek (*London*) (*communicated*): Lacau and Magat point out in their paper that a partially degraded polymer is less susceptible to degradation than a virgin one. I can confirm this observation. Experiments carried out on polystyrene in bulk-phase in presence of air over a temperature range from 180° to 220° lead to the conclusion that inhibitors are formed during degradation. This view is supported by experiments using a number of antioxidants and by experiments described in the paper by Votinov, Kobeko and Marei where the monomer produced during degradation was found not to effect polymerisation due to the presence of degradation products which acted as inhibitors. My experimental results can be quite satisfactorily accounted for by the following reaction scheme:

$$\text{Polystyrene} + O_2 \xrightleftharpoons{\text{Rapid}} \text{Polystyrene hydroperoxide}$$

Chain scission   Inhibitors

$$\downarrow$$

Decay of inhibitors.

The energy of activation for the initial part of the degradation was found to be 25·2 kcal.

Dr. M. Magat (*Paris*) said: We would like to add that since our paper was sent in, we have carried out a few preliminary experiments on the degradation of polymers in the absence of oxygen at temperatures above 200° C. In agreement with Grassie and Melville, we could observe *in vacuo* a degradation of GR-S in toluene solution at 210° and 240° C. Although our results are as yet qualitative, we can conclude that both postulated mechanisms, the thermal degradation of Taylor and Tobolsky and the oxidative breakdown of Farmer, coexist in the case of butadiene-styrene co-polymer, but that the latter is largely predominating at 70-140° C.

Mr. N. Grassie and Prof. H. W. Melville (*Aberdeen*) (*communicated*): Mr. Hall suggests that the mechanism of the degradation of polystyrene is such that there is a rapid breakdown to shorter chains which then degrade to monomer by splitting at the ends. Experiments have been carried out upon polymethyl methacrylate into whose chains small amounts of impurity have been incorporated in the form of monomeric acrylonitrile. It was then found that a rapid breakdown of large chains did indeed take place in the initial stages. In one particular case, a sample of such a copolymer was prepared which had a molecular weight of 600,000 and which contained one acrylonitrile unit to each 400 methyl-methacrylate units. The rapid initial fall in molecular weight tended to about 40,000 which one would expect if the breaks were occurring at the acrylonitrile units. Considering then the case of copolymerisation of oxygen with styrene, it may be that the rapid fall in molecular weight which Mr. Hall has observed is due to scission at oxygen links. Throughout our work here it has become very evident that small changes in structure have often a marked effect upon degradation characteristics and it is very important to define exactly the methods which have been used in the preparation of monomer and preparation of polymer.

Dr. Frank suggests, on thermodynamical grounds, that degradation is not likely to take place unless there was transfer in the polymerisation reaction. It seems fairly definitely established, however, that little or no transfer could have taken place under the conditions of preparation of any of our polymer samples. The other arguments of Dr. Frank had been considered but have been omitted from the paper for lack of space.

Dr. Dewar claims that in the initial stages of the reaction the mechanism is indeed reverse polymerisation through double-bond ends formed by disproportionation and later, when all double-bond ends have been eliminated, it becomes easier for scission to take place in the body of the molecule. Hence he explains the later fall in molecular weight. This does not explain, however, the very important fact that no fall in molecular weight takes place with low molecular-weight polymers and that the higher the polymer the sooner does its molecular weight fall away. Experiments have been carried out on polymer with a molecular weight of 740,000 and it has been found that the degradation curve is very accurately a diagonal in Fig. 1 (p. 379), and no part of the curve is strictly of the typical reverse-polymerisation type. This makes the solution more clear, because it is obvious that besides step degradation, the diagonal can also represent reverse polymerisation provided every molecule in which degradation is initiated, is terminated, at some point before it degrades completely.

It is obvious, then, that the whole case of the reaction of all samples is still reverse polymerisation but there is always the possibility of termination before complete disintegration. As the molecular weight goes up the chances of termination will increase and so the fall-away in molecular weight will occur sooner in the reaction. It is important to note, however, that the curve now falls below the diagonal—this would be necessary if the molecules split in two as Dr. Dewar suggests.

When molecules disproportionate a double-bond is left on one, and a single bond on the other, participating molecule. We agree with Dr. Dewar that the double-bond ends probably break first but it is certain that the single-bond ends also degrade, although with a higher energy of activation. It is the decrease in the number of easily broken double-bond ends and the greater stability of the single-bond ends which causes the marked decrease in rate and increase in the energy of activation of the reaction. It is also important to note that the energy of activation increases even when the molecular weight does not fall away, indicating again that the increase in energy of activation has nothing at all to do with the fall-away in molecular weight.

In reply to Prof. Price, we may point out the marked effect which end-groups have in the reaction and also the fact that this termination mechanism could not apply to photopolymer which would thus have an infinite molecular weight—this is not the case. Also in our dyestuff experiments, inhibition would form two molecules out of one and so the molecular weight would fall markedly in the initial stages—this was found definitely not to be the case.

Prof. M. G. Evans and Mr. J. H. Baxendale (*Leeds*) (*communicated*): A type of polymer degradation which has not been discussed in this section is that brought about by mechanical action on the polymer solutions. It has been shown that in solutions of poly-isobutene, the molecular weight of the polymer can be reduced by mechanical agitation of the solution.[9] Many workers [10] have shown that in solutions of polymers subjected to ultrasonic radiation an irreversible decrease in the molecular weight of the polymer results. At first sight it seems difficult to relate this mechanical breakdown to the rupture of a C—C bond. It seems clear, however, from work done at Leeds by Mr. Watson [11] and Mr. Hargrave [11] that the breakdown is not associated with an oxidation since mechanical degradation can be obtained in solutions from which oxygen has been rigorously excluded and in solutions containing anti-oxidants. The rate of molecular-weight decrease increases with increasing rate of shear of the solution. From experiments on molecular-weight distribution before and after mechanical breakdown, and the influence of chain-stopping agents such as iodine, the work of Mr. Hargrave [11] would suggest that the mechanism of breakdown does not involve the primary rupture of the polymer chain leading to free radicals which by their re-combination could lead to a lower molecular-weight distribution, nor does an oxidative attack of the C—C bond to produce peroxide groups, appear to be the mechanism. Another puzzling feature of this system is the comparatively small effect which increase in temperature has upon the rate of degradation.

We present these observations here because this is the type of degradation for which at the moment there appears to be no adequate explanation.

[9] Thomas *et al.*, *Ind. Eng. Chem.*, 1940, **32**, 299.
[10] Freundlich and Gillings, *Trans. Faraday Soc.*, 1938, **34**, 649; Mark, *J. Acoust. Soc. Amer.*, 1945, **16**, 183.
[11] Watson, *Thesis* (Leeds), 1945; Hargrave, *Thesis* (Leeds), 1947.

Contents

AUTHOR INDEX*

* The references in heavy type indicate papers submitted for discussion.